Computer-aided process operating strategy

Reddy, S.

Award date:
1987

Awarding institution:
University of Bath

COMPUTER-AIDED PROCESS OPERATING STRATEGY

Submitted by : S. Reddy
for the degree of Ph.D
of the University of Bath
1987

COPYRIGHT

S. Reddy

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

CONTENTS

ACKNOWLEDGEMENTS

The author sincerely thanks all those who have contributed to this work. He is specially grateful to the following persons and organisations:

1. Dr. P.L. Yue for his supervision, advice and help.
2. The University of Bath and ICI Plc for financial support.
3. Mr. P. W. J. Chandler, Dr S. Craig, Mr. A. J. Treadgold, and Mr. K. Whalley of ICI Plc for their advice and help.
4. To my wife and daughter for their unfailing support and understanding.

This thesis is dedicated to my parents.

SUMMARY

One of the major preoccupations of the operating personnel in process industries has to do with monitoring and sustaining economic and safe running of process plants. An important target is to operate the plant close to its optimum conditions with respect to production rates and/or raw material and energy consumptions without compromising safety or environmental standards. The actual optimum conditions are affected by constraints which are unique to a process and site conditions and may be different from those specified by the design. There is therefore a need to ascertain the actual optimum conditions of the plant and develop a strategy for optimisation.

A computer-aided optimisation system has been developed to aid the operation of a nitric acid plant. The system is designed to optimise plant performance by validating process information, executing a process simulator and suggesting operating strategy to attain optimum process conditions. The simulation program is based on steady-state models which have been validated by matching model prediction with plant data. The optimisation program works out the optimum operating conditions based on parametric models developed from the simulation studies. If there is deviation of the actual operating conditions from the achievable optimum, remedial operating strategy will be recommended to the operating personnel.

The methodology of optimising plant operation proposed in this research broadly consists of the following steps:

1. Validating the measurements recorded by the on-line database which are required as inputs for running a process simulator. The validation is carried out by using mathematical mass balance reconciliation and rules in a

knowledge-base.

2. Matching the rest of the on-line database data with that predicted by a tuned process simulator, checking on their validity.

3. Using the relevant validated database information in optimisation algorithms to maximise the efficiency of running the process plant.

4. When deviations between the actual operating conditions and optimum (and achievable) conditions are detected, remedial action is suggested to the operating personnel who can then make changes in the operating strategy or parameters.

The research is conducted in collaboration with ICI Plc, Chemicals and Polymers Group at Severnside, Bristol. Whereas the metholodology is in the first instance implemented at two of their Nitric Acid Plants which are of identical capacity and design, it can be extended to other processes and plants.

The benefits of using the above methodology are:

1. It helps to optimise the operation of the process with respect to raw material and energy consumptions, whenever there are planned changes in production rates.

2. Information collected by the on-line databases is scrutinised and validated, thus preventing incorrect deductions or decisions being made.

1.0 Introduction

Computers have long since become a very powerful tool to assist engineers in the practice of chemical engineering. The various areas of chemical engineering that computing has been applied to are process design, project engineering, process control, optimisation and resource management. Computer systems which were once prohibitively expensive are now availible cheaply and in many different configurations to meet the diverse needs of the chemical industry. The ever reducing costs of hardware has encouraged industries to further apply and rely on computers for their day to day operations.

1.1 Computers in Process Design, Engineering and Construction.

In the last two or three decades there has been tremendous progress in the field of computer aided process design and engineering. The areas of application are in process flowsheeting, equipment design and drafting.

Computer aided engineering (CAE) systems according to Canfield (Canfield, 1985) are integrated computerised methods for handling information and calculations required for an engineering task at hand. Alper (Canfield, 1985) pointed out that CAE systems for process plants can be divided into two parts which are the CAE front-end and back-end that are separarted by a computer aided design (CAD) function. The front-end CAE incorporates those tasks that precede the preparation of a plot plan; then the CAD part is used to produce the dimensional representation of the process plant. The back-end CAE part covers all aspects of mechanical, civil and electrical design that are required to

transform the process designs produced by the CAD effort into the process plant.

The increasing use of computers in the design and detailed engineering of chemical plants has had a benefical effect on the cost and safety of process plant equipment and also in bringing down the design and engineering costs of contracting firms. A number of steady state and dynamic flowsheeting packages have been developed since the late fifties. Several commercial packages available are discussed in detail by Leesley (Leesley,1982a). Today, before finalising the flowsheet of a process, designers study the various flowsheet options available to them to check factors such as raw material and utilities consumptions, process operability and control using both steady state and dynamic simulation programs. Most contracting firms in the business of building chemical plants use computer programs for detailed design (including mechanical design) of process units such as heat exchangers and fired heaters, columns and reactors. Standards such as TEMA (Tubular Heat Exchanger Manufacturers' Association), ASME (American Society of Mechanical Engineers) or British Standards can be specified while carrying out the design. Several packages that can carry out the layout and design of process piping are now available. The "Pipe Design Management System" or PDMS (Leesley, 1982b) is an example of a process piping design package. Some of these packages are capable of generating information that is required for preparing a bill of material for procurement, or carrying out civil engineering design and plant layouts. Design drawings are interfaced with drafting packages which prepare fabrication drawings required for the manufacturing of the equipment. The use of CAD has contributed to better utilisation of manpower, reducing the

number of engineers and draftsmen required for a project. Draftsmen, whose main duty in the past was drafting, now use CAD packages to carry out routine design of simple equipment, for example, unsophisticated pressure vessels, etc., a task which otherwise would have been done by the specialist engineer. The requirements of hardware for CAD have been discussed by Harrow (Harrow, 1983) who highlighted the factors to be considered before selecting a CAD system .

The availability of cheap personal computers has brought a revolution to computer aided drafting. Most CAD packages in the past were written to run solely on mainframe computers. However an increasing number of packages are now being made available for use on personal computers. In a recent article Bullock (Bullock, 1987) compared "traditional" CAD packages that are implemented on mainframe computers with those on personal computers. His study showed that PC based CAD systems are two to three times more cost effective than the "traditional" mainframe systems.

Future trends in computer aided engineering are aimed at the integration of software and engineering data that engineers commonly use. Many firms are integrating stand-alone design programs to avoid difficulties of keeping track of large quantities of programs and data, duplication of data and high software maintenance costs. Systems are being developed where engineers will be able to share data and have better access to it using database and networking technology. Another area where there are developments taking place is in providing on-line information to engineers using bibliographic and numerical databases.

1.2 Computers in process control and optimisation.

The primary operating objective of a chemical process plant is efficient and safe production. Production is concerned with attaining the specified quality and quantity of product. For a process to be economical and competetive, production with minimum costs is required. However the production plant must operate safely to avoid any hazards to the operating personnel or the environment.

Most computer based process control systems directly contribute to the above goals. By implementing process data aquisition systems the process can be continuously monitored to keep the raw material and utility consumptions of a process to the minimum. Computer based warning interlocking and surveilliance systems have positively enhanced the safe running of many hazardous processes. Through digital or microprocessor based regulatory control of the process engineers can now control processes closer to the optimum conditions than has been possible through manual control. There has been some concern and discussion about the gap between the advances made in the theory of computer based control and its practice in achieving business goals. However today there seems to be a rapid progress in this front because of the competetive nature of the chemical and hydrocarbon industries. Since the oil embargo of 1973 considerable effort has gone into the optimisation of energy systems. Steam balance calculations for steam systems having boilers, turbogenerators, deaerators, feedwater heaters etc. are now routinely carried out to optimise the generation and distribution of steam (Cleary, 1983).

An attempt of direct digital control (DDC) in a chemical plant was made in the early 1960s by ICI in collaboration with Ferranti Computers at Fleetwood in

the U.K. (Bennett and Linkens, 1982). Since then the field has been rapidly advancing with the introduction of the microprocessor. In the early seventies when minicomputers became much more commonly available than before, offline optimisation was considered adequate because of the difficulties in online optimisation. However, today online control of chemical processes is gaining popularity because of the lack of enforcement of action recommended by the offline optimisers, the time lag in making the changes.

Latour (Kane, 1980) cited some of the benefits of process optimisation as follows:

(1) Improved yields and /or quality

(2) Reduced energy consumption and operating costs

(3) Increased capacity of equipment

(4) Less maintenance cost

(5) More efficient engineers and operators

(6) Tighter and lower cost process designs

According to Barsamian (Barsamian, 1986) the feedstock costs of a 100,000 bbl/day petroleum refinery of medium complexity in Western Europe is around 900 million dollars . If computer optimisation can increase the yield by 1% the annual savings would be an impressive 9 million dollars. It is estimated that with advanced optimisation schemes, interunit coordination and optimised planning and scheduling, as much as 60 million dollars could be the potential economic returns for a refinery of the above capacity (Williams, 1983). Shell UK's experience in using an optimisation package "Process Operating and

Supervisory System" has been described by West (West, 1985). A 50% reduction in quality giveaway and substantial savings in energy by operating columns at reduced pressures and balancing heat exchanger networks were obtained.

Bashan described the implementation of a microcomputer based control system for the manufacture of acrylic resin by a batch polymerisation process (Bashan and Handelsman, 1987). The system involved using programmable controllers to control the input/output functions and execute sequential steps of the batch process and a microcomputer to oversee the product "recipes" and the process operation. According to these authors the plant operated more efficiently than the conventionally controlled plant and also consistently produced a product of superior quality.

As process information is the basis of any optimisation procedure it is important to prevent decisions from being taken on the basis of inaccurate information. This requirement is more critical for process optimisation because process optimisation activities are based on small improvements in process performance (Mah et al., 1976). Due to the very large scale of operation in most chemical processes today, the impact of any error in data used for optimisation may be greatly amplified in terms of monetary losses.

The selection and design of process control software which converts a computer system that is physically wired to sensors, controllers, and valves into system that helps an operator to run the plant is very important. Many tasks can be achieved by using commercially available software. There are advantages in using commercial software providing care is taken to ensure that the requirements of the plant are not compromised for the sake of adapting the

software together with its limitations.

1.3 Miscellaneous applications.

An area where computers have played a major role in process plant construction is in project engineering by monitoring the simultaneous and sequential tasks in the construction of large process plants. The Program Evaluation and Reviewing Technique (PERT) is an example of a method available for this purpose (Fourre, 1968). Present day process plant construction work can be divided into several hundred and sometimes even thousands of individual activities. It would therefore be almost impossible to keep track of these activities without the help of a computer generated PERT charts.

Computer surveilliance and monitoring of the equipment are important applications of the computer in the chemical and nuclear industries. Surveillance and monitoring activities include corrosion and condition monitoring. Corrosion testing can be done using electric resistance, potential measurements and Doppler tests. Condition testing in the case of rotating equipment is carried out by monitoring and recording data by a data aquisition system. For example, the vibration levels in the various components of the rotating equipment, such as shaft bearings, the level and frequency of vibrations measured at various locations indicate the conditions of the components (Hines, 1977). It is now a standard practice to have microprocessor based monitoring of the bearings of high speed centrifugal compressors in a system incorporating sensors, instrumentation, alarms and safety interlocks.

A recent use of computers in the chemical industry is in expert systems

which are defined as computer programs that are programmed with knowledge of experts and can be consulted when needed by users who are seeking advice in problem solving. Expert systems have been suggested to help operators to diagnose faults in process plants (Koukoulis, 1985), and to operate the cement process more efficiently. Kerridge showed how to construct a simple expert system to troubleshoot a decreased product rate in a distillation setup consisting of a distillation column, overhead condenser, reflux drum and pump and a reboiler (Kerridge 1987). Expert systems have also been used for advising maintenance personnel. Several hydrocarbon processing industries are moving towards knowledge based maintenance procedures (Finley, 1987).

1.4 Objectives of the Research.

One of the major preoccupations of the operating personnel in process industries has to do with monitoring and sustaining economic and safe running of process plants. An important target is to operate the plant close to its optimum conditions with respect to production rates and/or raw material and energy consumptions without compromising safety or environmental standards. The actual optimum conditions are affected by constraints which are unique to a process and site conditions and may be different from those specified by the design. There is therefore a need to ascertain the actual optimum conditions of the plant and develop a strategy for optimisation.

This research presents a methodology for the collection of process information, its validation, followed by its use in the optimisation of plant operation. The methodology is described broadly here in general terms. Fig. 1.1 shows the flow of information

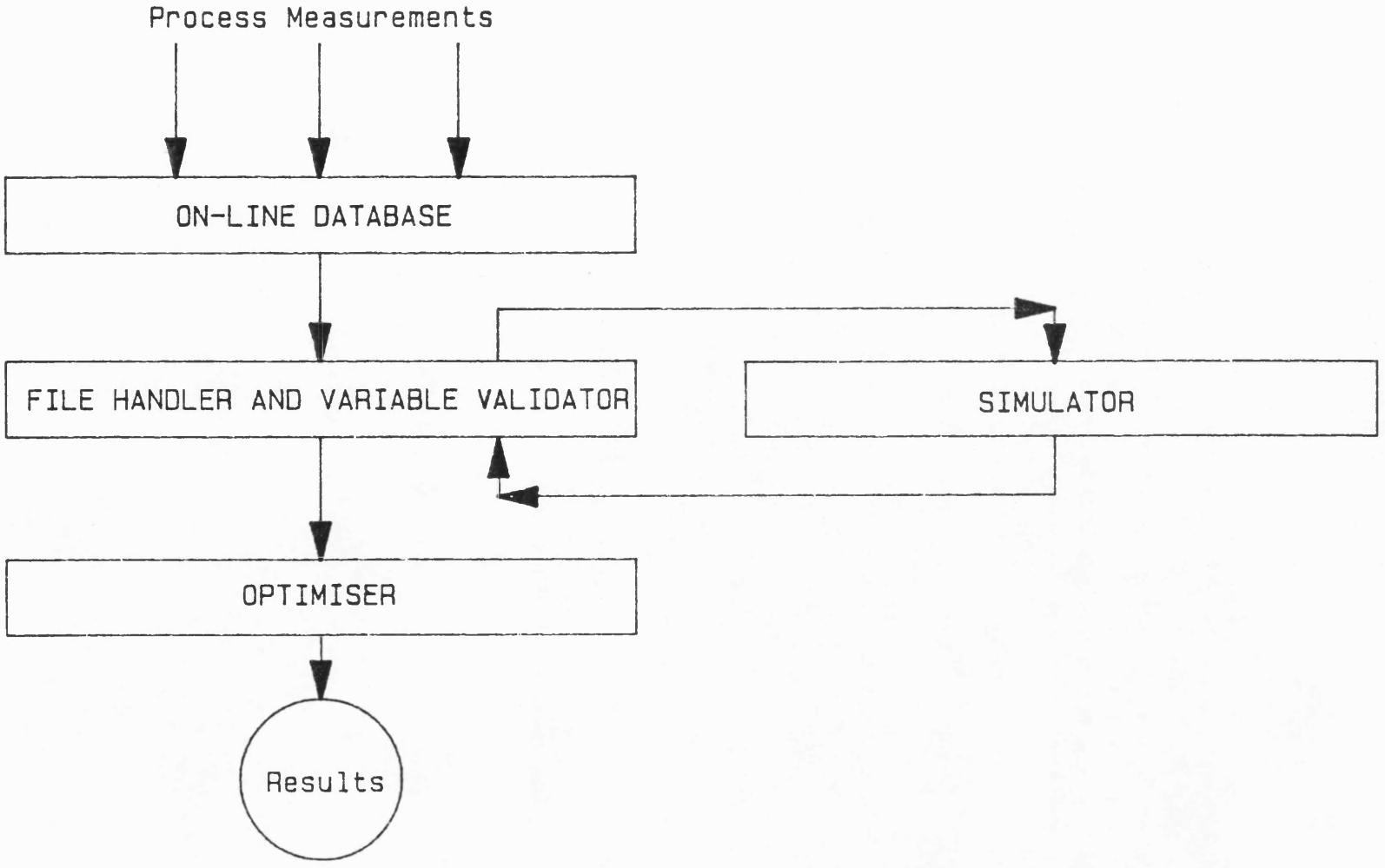


Fig 1.1 The methodology

The methodology requires a plant on-line database which acquires plant data and a computer program which simulates the steady state operation of the plant with acceptable fidelity. The steps are then followed:

1. The validation of those data recorded by the plant database which are required as inputs for running the process simulation program (to be called the SIMULATOR hereafter). Instrument errors and equipment faults are filtered out, thus putting the process simulation on a sound basis.

2. Matching the rest of the data in the plant database data with those calculated by the process SIMULATOR. The validity of these data is therefore checked and corrections made where appropriate.

3. Using the relevant validated database information in optimisation algorithms to maximise the efficiency of running the process plant.

4. When deviations between the actual operating conditions and optimum (and achievable) conditions are detected, remedial action is suggested to the operating personnel who can then make changes in the operating strategy.

1.5 The organisation of the thesis.

Chapter 2 of the thesis covers a literature survey on nitric acid process technology, chemical process simulation, data aquisition systems and data validation, expert systems and optimisation.

The simulation of the nitric acid process is dealt with in Chapter 3 and includes details on the architecture of the SIMULATOR, the physical properties package and individual process unit modules.

Chapter 4 describes software called the AUDITOR, which is responsible for the process variable validation and traces the flow of information to the

SIMULATOR and OPTIMISER from the AUDITOR.

Chapter 5 of the thesis discusses the program called the OPTIMISER which is used for optimisation of the process units. Chapter 6 presents and discusses the results of process optimisation.

Conclusions and recomendations for future work are presented in chapter 7. The source codes of the various programs are included in the Appendicies.

2.0 A BRIEF OVERVIEW OF SOME RELEVANT PRIOR WORK

2.1 Nitric acid process technology

Nitric acid is an important inorganic acid produced on a large scale to meet the requirements of the fertiliser, explosives and organic synthesis industries. The nitric acid process technology has been constantly improved from the days of using nitrates as raw material to present day processes based on the oxidation of ammonia incorporating innovations of energy recovery.

2.1.1 Historical background

Nitric acid was known to alchemists as Aquafortis, or strong water, and was used to make aqua regis, a mixture of sulphuric and nitric acids, which was used to dissolve gold.

The earliest description of the manufacture of nitric acid was by Arabs in the 8th century (Kirk and Othmer, 1985a). It was produced by the reaction of alum or vitroil with saltpetre. Nitric acid, being volatile was removed by heating and recovered by condensation.

$$6NaNO_3 + Al_2(SO_4)_3.K_2SO_4 + H_2O = 6HNO_3 + Al_2O_3.4Na_2SO_4 \quad .....(2.1)$$

$$2NaNO_3 + CuSO_4 + H_2O = 2HNO_3 + Na_2SO_4 + CuO \quad .....(2.2)$$

Large deposits of saltpetre, or sodium nitrate, were discovered in Chile and was commonly known as Chile Saltpetre. By reacting a mixture of saltpetre and sulphuric acid at 150 C, nitric acid was produced, then distilled and recovered by condensation in earthenware pipes and vessels (Martin and Barbour, 1915). The ratio of saltpetre to acid was maintained to form sodium

hydrogen sulphate instead of sodium sulphate as the latter reaction requires a higher temperature to proceed.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3 \quad \text{.....(2.3)}$$

Brikeland and Eyde were the first to produce nitric acid using an electric arc process and several plants were built in Norway where inexpensive electricity was available to run the arc furnaces. In the presence of an electric arc nitrogen and oxygen in air combined to form nitric oxide (Pratt and Noyes, 1965) which was then cooled, oxidised and absorbed to form nitric acid. The temperature of the arc was measured at 3600 K, yielding 5-6% v/v nitric oxide. To eliminate the backward reaction, the gas was quenched with cold air to bring the temperature down to 1300 K.

The catalytic oxidation of ammonia over platinum gauze was patented by Kuhlmann (Keleti, 1985 a) in the year 1838. The first technical scale plant to produce nitric acid was set up at Gerthe, near Bochum in 1906. The catalyst used at this plant was a roll of corrugated platinum strips about 2 cm in width. However, catalyst of this type was consumed in very large quantities per unit of acid production, and its life was short.

Kaiser (Hunt, 1958), who filed his patents in 1909 used platinum gauze for ammonia oxidation. The process involved the preheating of air to 300-400 C and passing the ammonia-air mixture over layers of gauze of 0.6 mm diameter and 1024 mesh size, which until today remains the standard diameter and mesh size used.

High tonnage production of nitric acid began in the 1920's when the

synthetic ammonia industry came of age by the widespread use of the Haber's process for ammonia.

It was after the invention of stainless steel in the 1920's that the nitrogen oxide absorption process was conducted at pressures higher than atmospheric pressure resulting in reduction of equipment sizes and increased absorption efficiencies (Busby, et al., 1978).

2.1.2. Ammonia Oxidation

The overall equation for the oxidation of ammonia is as follows:

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad \Delta H_R = -907.2KJ/gmol \qquad .....(2.4)$$

The oxidation of ammonia is one of the efficient catalytic reactions known. The reaction time is in the order of 10^{-11} sec (Holzmann, 1967). As the reaction time is so low the rate controlling step is the supply of reactants to the catalyst surface.

There are also a number of possible side reactions depending on reactor conditions:

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O \quad \Delta H_R = -1104.9KJ/gmol \qquad .....(2.5)$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \quad \Delta H_R = -1269KJ/gmol \qquad .....(2.6)$$

$$4NH_3 + 6NO = 5N_2 + 6H_2O \quad \Delta H_R = -1810.8KJ/gmol \qquad .....(2.7)$$

Several theories have been put forward to explain the mechanism of reaction (2.4), the three most important ones are :

1. The imide theory (Zawadski, 1950) was developed by Raschig and further

by Zawadski who proposed that ammonia reacts with an adsorbed oxygen atom to form the imide by the reaction:

$$NH_3 + O = NH + H_2O \quad \text{.....(2.8)}$$

Nitric oxide is subsequently produced by the reactions :

$$NH + O_2 = HNO_2 \quad \text{.....(2.9)}$$

$$4HNO_2 = 4NO + 2H_2O + O_2 \quad \text{.....(2.10)}$$

2. The nitroxyl theory (Andrussow 1924 and 1926), was proposed by Andrussow. Contrary to the view that adsorbed oxygen is in the atomic form, he suggested that ammonia reacts with molecular oxygen :

$$NH_3 + O_2 = HNO + H_2O$$

$$HNO + O_2 = HNO_3$$

3. The hydroxylamine theory was proposed Bodenstein (Bodenstien, 1937), who suggested that hydroxylamine was formed as an intermediate compound according to the equation :

$$NH_3 + O = NH_2OH$$

This was followed by the reactions :

$$NH_2OH + O_2 = HNO_2 + H_2O$$

$$4\ HNO_2 = 2\ H_2O + O_2 + 4\ NO$$

This theory was supported by the experimental results which showed that hydroxylamime was present in the gaseous product.

Experimental work carried out by Andrussow (Andrussow 1924 and 1926) showed that the transport of ammonia to the platinum surface was the rate determining step. Satterfield and Cortez correlated mass transfer data on woven

wire catalysts to arrive at mass transfer coefficient for calculating the rate of transfer of ammonia to the catalyst surface (Satterfield and Cortez, 1970). Using the mass transfer coefficient estimated by the Satterfield and Cortez correlation, the conversion of ammonia to nitric oxide using a platinum gauze pack can be estimated according to the procedure given by Rase (Rase, 1968).

2.1.3 Absorption of nitrogen oxides

The absorption of nitrogen oxides by water involves absorption accompanied by chemical reaction. There are several uncertainties about the reaction mechanism, due to the complexities resulting from the mass diffusion in the vapour and liquid phases. Several workers (Brotz and Schur, 1957, Sherwood and Pigford, 1952, Dekker et al., 1957, Chilton, 1960, Dekker et al., 1961, Hesky, 1961, and Koukoulik and Marek, 1968) have used simplified kinetics and mass transport equations in modelling NO_x absorption.

Andrews and Hanson were the first to attempt to combine chemical reaction rate, reaction equilibrium and mass transfer into a rigorous model for the absorption of nitrogen oxides (Andrews and Hanson, 1961.). Ten possible mechanisms were considered and studied by them. They concluded that at high concentrations of nitrogen oxides in the vapour, the controlling mechanism was the dissolution of N_2O_4 and its hydrolysis thereafter to HNO_3 and HNO_2. At low concentrations of nitrogen oxides, the control is either the diffusion of NO_2 through the liquid film or the absorption of HNO_2.

2.1.4 Commercial nitric acid processes

All processes for the production of weak nitric acid are very similar except for the pressure of operation. The pressure levels can be broadly classified into atmospheric, medium pressure (3-5 bar) or high pressure (7-12 bar) processes.

Processes for nitric acid can be divided into two categories :

1. Mono-pressure Process

2. Dual-pressure Process

In the mono-pressure process, both the oxidation and absorption are carried out at the same pressure, whereas in dual pressure processes the absorption is carried out at a higher pressure than the oxidation stage. Both these processes are equally widely used. A comparative study of the mono-pressure and dual pressure processes made by Harvin et. al., (Harvin, 1979) concluded that while the dual pressure process has a distinct advantage with respect to its lower ammonia consumption and catalyst usage, the single pressure process has a lower capital cost and is more energy efficient in terms of steam generation and has a lower heat rejection or cooling requirement. Hence, the choice of process would depend on the unique circumstances or requirements of a particular plant-site, such as need for steam, space, and ammonia costs.

A recent review (Keleti, 1985 b) of the various commercial processes for the manufacture of technical grade dilute nitric acid gives process, equipment details and flowsheets. Other papers (Hopfer and Dayasager, 1980; Conner and Niezgoda, 1979) give details of innovations made in recent years to enhance

ammonia efficiency and energy recovery.

2.2 Process simulation

Simulation can be defined, according to Kirk and Othmer (Kirk and Othmer, 1985a), generally as the use of a system, usually a digital computer, to mimic the behaviour or actions of another. Another definition, according to Shannon, is "the process of designing a computerised model of a system (or process) and the conducting of experiments with this model for the purpose of understanding the behaviour of the system or evaluating the strategies for the operation of the system" (Shannon, 1975).

The reasons why one may want to simulate a system may be (Kirk and Othmer, 1985b) :

1. The system may not yet exist.
2. The knowledge about the system may be insufficient.
3. The system may be too time consuming, costly or dangerous to operate.

Shannon, in the above reference, listed the various steps of a simulation exercise. They are:

1. The formulation of a precise mathematical model of the system under consideration.

2. Converting the mathematical model into a computer program using a suitable programming language.

3. Validation of the results derived by running the program to check the

fidelity of the simulation.

4. Executing the model on the computer for data generation for purposes including the design of experiments to be carried out.

5. Interpretation of results to achieve the intended purpose of the simulation.

6. The documentation of the study and its results.

2.2.2 Chemical process simulation

The first developments in the field of chemical process simulation took place in the late 1950s (Kesler and Kessler, 1958). According to Westerberg et. al., (Westerberg, 1979.) the first fifteen-year period of development could be divided into three five-year periods. The first covered work in between 1955 and 1959, when computers were small and slow and before any high level language such as FORTRAN was developed. The size of programs during this phase of development was small and limited to performing the simulation of a single equipment. During the next five years several commercial simulators appeared, some of these survived the period and are in use even today. These programs were based on high level languages such as FORTRAN. They have proper physical property prediction routines, and put together in a modular manner. In the period of 1965 to 1969 computer size and speed were rapidly enhanced. The simulators that were developed in the previous period were put to the test and several of them failed to be successful. By the early seventies several companies began recognising the fact that process simulation packages were time-saving and cost effective. In the early eighties, with rapid developments in the field of

personal computers, simulation programs were developed for use on desktop computers. These programs were much more user friendly than the ones offered previously, making them less forbiding for non specialist-process engineer to use.

Process simulation programs can be divided into two categories:

1. Steady state simulation programs.

2. Dynamic simulation programs.

Steady state programs assess the steady state operation of a process and can be represented by a set of linear and non-linear algebraic equations which describe the steady state behavior of a system. Although, the solution of these equations is more straightfoward than in the case of a dynamic model, it may be necessary to carry out several simulation "runs" before the behaviour of the process can be studied at turndown capacities.

The architecture of steady state simulators could either be of sequential modular or simultaneous modular type. The sequential modular method calculates the performance of the process module by module where each module represents a process operation such as mixing, heat exchange, distillation etc. On the other hand the simultaneous modular approach solves all the equations or modules simultaneously to speed up the solution and allow easy integration of design constraints (Rosen 1979, Umeda and Nishio, 1972). Westerberg et. al. have made a comparison of the two approaches (Westerburg et.al., 1979).

Examples of some important steady state simulators in use today are listed in Table2.1, below.

	Simulator	Type	Reference
1	FLOWPACK II	Psuedo-Sequential	Berger and Perris, 1979
2	FLOWTRAN	Sequential	Rosen and Pauls, 1979
3	PROCESS	Sequential	Leesley, 1982c
4	ASPEN	Sequential	Evans, 1979
5	CHESS	Sequential	Motard and Lee, 1971
6	GEMCS	Sequential	Johnson and Peters, 1979
7	CONCEPT MARK 4	Sequential	Winter, 1982

Table 1. Steady state simulation packages.

Dynamic simulation programs which predict the dynamic behaviour of a processs require the solution of a set of differential equations. The dynamic nature of chemical processes is due to possible changes in rates or quality of raw materials and utilities. Thus dynamic simulation is used for the study of their plant behaviour during start-up, shut-down and changing of operating variables and feedstocks. Dynamic simulation also helps to study the effects of possible hazards on the safety and performance of the process.

Examples of dynamic process simulation packages are given in Table 2.2 below:

	Simulator	Reference
1	DYNAMIC FLOWPACK II	Berger and Perris, 1979
2	DYNSYS	Rosen and Pauls, 1979
3	MODSYS	Leesley, 1982d
4	BOSS	Joglekar and Reklaitis, 1984
5	DIVA	Marquardt et al., 1987

Table 2.2 Dynamic simulation packages.

Some examples of dynamic process simulation studies reported in the literature are listed in Table 2.3 below:

	Example	Reference
1	Dynamics of reactor	Stewart, 1980
2	Distillation control	Shinsky, 1977
3	Extraction control	Patterson and Rossa, 1980
4	Polymerisation Reactions	Overturf, 1978
5	Batch reaction control	Lackmeyer and Kempfer, 1977

Table 2.3 Dynamic simulation studies.

2.2.3 Physical property and Thermodynamic Packages

A prerequiste of a good process simulator is the robustness and accuracy of the physical property and thermodynamic prediction capability. An exhaustive survey and recommendations of the methods to be used is given by Reid et. al. (Reid et. al., 1973). It is estimated that some 70% of the processing time consumed in certain simulation calculations is taken by the thermodynamic package (Westerberg, 1979). Because of the great diversity of chemical processes no databank can possibly hold all the data that are required for simulating any chemical process at random. A list of databanks that are available to industry and universities was listed by Fair (Fair, 1980).

2.3 Data acquisition systems and validation

Data acquisition systems in the fifties were mostly of the analogue type. Distributed digital systems capable of logging massive amount of data are now being used in several hydrocarbon and chemical industries. The objective of data acquisition was to keep a closer watch on the process by providing the following information :

1. Historical and current data of the process measurements being logged.

2. Graphical displays of trends of chosen variables to study the effects of phenomena such as fouling, catalyst deactivation, etc.

3. Economic performance of the process.

Springell explained the use of data acquisition and database systems in the real-time economic performance control of chemical processes (Springell, 1985). The salient features of several commercially availible plant data acquisition systems have been described in a recent review (Kane, 1987).

It is important to validate data collected by the data acquisition systems. Some of the data acquisition systems described in the above review do have their own material balance validators. Himmelblau reviewed the various methods availible for mass balance reconciliation (Himmelblau, 1985). However only a few of the methods availible are capable of handling non-linear material and heat balances material balances which is the case with many flowsheets.

2.4 Expert Systems

An expert system was defined by Bramer as a computing system that embodies organised knowledge concerning some specific area of human

expertise, sufficient to perform as a skillful and cost effective consultant (Michie, 1983). They allow for accumulated experience, judgement, and heuristics of an expert to be incorporated into an automated reasoning system, which can be used by non-experts for consultation while solving problems.

2.4.1 Structure of expert systems

An expert system consists of the following components (Sriram, 1985) :

1. Knowledge Base, which is a collection of general facts, heuristics, IF-THEN rules, and in some cases knowledge of uncertainty factors.

2. Context, which is a workspace for keeping track of the solution process.

3. Inference Engine, which uses the knowledge base and the context to come up with solutions.

4. In addition to the three main components, above, the expert system should also have a user interface, an explanation facility, and a knowledge acquisition facility.

2.4.2 Examples of expert systems

Some general examples of expert systems are:

1. DENDRAL, an expert system for working out the structure of chemical compounds (Lindsay, 1980).

2. MYCIN, for diagnosing baterial infection (Shortliffe, 1976)

3. PROSPECTOR, for carrying out geological exploration and evaluation (Duda, 1978).

4. CASNET, for diagnosis of glaucoma, an eye disease (Kulikowski, 1982).

5. MOLGEN, for design of genetic experiments (Alty, 1984).

6. INTERNIST, for acting as a diagnostic consultant for general internal medicine (Miller, 1982).

The potential of expert systems being applied to chemical engineering senarios was identified in 1983 (Motard, 1983, Sargent, 1983 and Umeda, 1983).

Examples of expert systems in chemical engineering are:

1. CONPHYDE (Banares-Alcantara, et al. 1985) is an expert system for recommending the most suitable equation of state for a given system of chemical components. It contains about 37 heuristic rules which covers six equations of state. CONPHYDE prompts the user for information on the components, composition and other physical conditions of the chemical mixture. The program outputs grades the six equations of state in order of decreasing applicability.

2. FALCON (Chester, 1984) can be used for diagnosing faults in process plants.

3. PICON (Moore, 1984) is used for monitoring and controlling industrial processes. Knowledge from the expert process operator and process engineer are incorporated into the knowledge-base. In addition PICON can also use mathematical model based knowledge (deep knowledge) to control the process.

4. HEATEX (Grimes, 1982) is an expert system for configuring heat exchanger networks which minimise energy consumption by suggesting heat exchange matches between the various process streams. HEATEX is written in a language called OPS5 (Forgy, 1981) which is a rule-based programming language.

5. DECADE is an expert system for the selection of catalyst for a specified single

step reaction. (Banares-Alcantara, 1985)

6. ESVS is an expert system for the selection of valves for different process services (Norman and Voon, 1985).

7. REACT is used for charting out synthetic routes for the production of various industrial chemicals (Govind and Powers, 1981).

It has been suggested that expert systems can be used for process plant start-up (McGreavy, 1985) and for process plant maintenance (Efsthathiou, 1985). Haspel and Taunton discussed the application of a rule-based control system in cement kiln operation (Haspel and Taunton, 1985). According to them, the knowledge based supervisory control of cement kilns was far more successful than the previously tried conventional algorithmic methods.

Andow (Andow, 1985) used the application of expert systems in fault diagnosis in chemical processes and came to the conclusion that the use of expert systems is not straight forward because of the following:

a. Not all plant states are observable.

b. Instrument failures are common and can cause confusion.

c. The analysis must consider dynamic behaviour of the plant, the rules are not all static.

d. The monitoring and display systems used by the operator may be difficult to use effectively for fault diagnosis even though they may be perfectly suited to normal operation.

Palowitch and Kramer discussed the architecture of an expert system for fault diagnosis of chemical plant faults, which identifies the primary process

variable deviation and the expert system then prepares a list of the various faults that could cause the deviation and suggests remedial action (Palowitch and Kramer, 1985).

2.5 Process Optimisation

According to Peters and Jelen optimisation which is the urge for efficiency has a basic psychological origin. The human mind can confront a task or problem and recognize more than one course of action, followed by a second phase, the selection of what is considered the best action. The two steps taken together, i.e. the recognition of alternatives and decision form the process of optimisation (Jelen, 1970).

Almost any problem in design, operation, analysis of manufacturing plant or process and associated problems such as production scheduling can be reduced to the determination of the largest or smallest value of a function of several variables (Beveridge and Schechter, 1970). The procedure of maximising or minimising a function of one or several process variables that affect the economics of the process is called process optimisation.

Using the fundamentals of calculus, one can locate the extremum of a design objective function, by differentiating the function with respect to the design variable, equate the derivative to zero and solve the equation for the design variable (Hancock, 1960). However this method has its limitations because most design problems are based on functions that may not lend themselves to easy manipulation or they may be discontinuous. We then have to

resort to numerical search methods for optimisation. In the case of optimisation of a unimodal function with a single design variable one can use region elimination. The Golden section or Fibonaccian search methods (Rudd and Watson, 1968a) are two examples.

Many optimisation problems in industry are of the multivariable type. There are many methods available for the optimisation of constrained or unconstrained multivariable objective functions. However the optimisation problems faced in this research are of the single variable type as can be seen in Chapter 5 and can be solved with any one of the simple methods described above.

3.0 THE SIMULATOR

In the subsequent sections the requirements, choice and development of the SIMULATOR will be discussed.

3.1 Description of the nitric acid process to be simulated

Fig. 3.1 shows a schematic flowsheet of the nitric acid plant. Atmospheric air is compressed to approximately 5.0 bar by an axial compressor, and is used to reheat tailgas from the absorber in the tailgas heater where the air is split into two streams. The first stream, which is the major stream, is fed to the gas-mixer as "primary" air where it is mixed with ammonia gas from the ammonia vaporiser. The second air stream called "secondary" air is used for "bleaching" the product acid prior to the acid being sent to storage.

The mixed gas is then filtered and fed downwards into the oxidation reactor (referred to in the industry as the burner) which has several layers of platinum-rhodium gauze. Ammonia is oxidised to nitric oxide catalytically by air in the burner. The conversion of ammonia to nitric oxide that can be achieved is between 90 to 96%. The converted gas leaves the converter section at around 870-890°C and enters the waste heat boiler which is directly below the converter. Here the gas is cooled to around 210-230°C, recovering heat to raise superheated steam at approximately 21 bar and 315°C.

Process gas exiting from the waste heat boiler is then cooled further in a boiler feed water preheater and in a gas-cooler to around 45°C before passing on to the absorption towers. The cooling produces a 35-40 % acid condensate which is sent to the absorption system for enrichment.

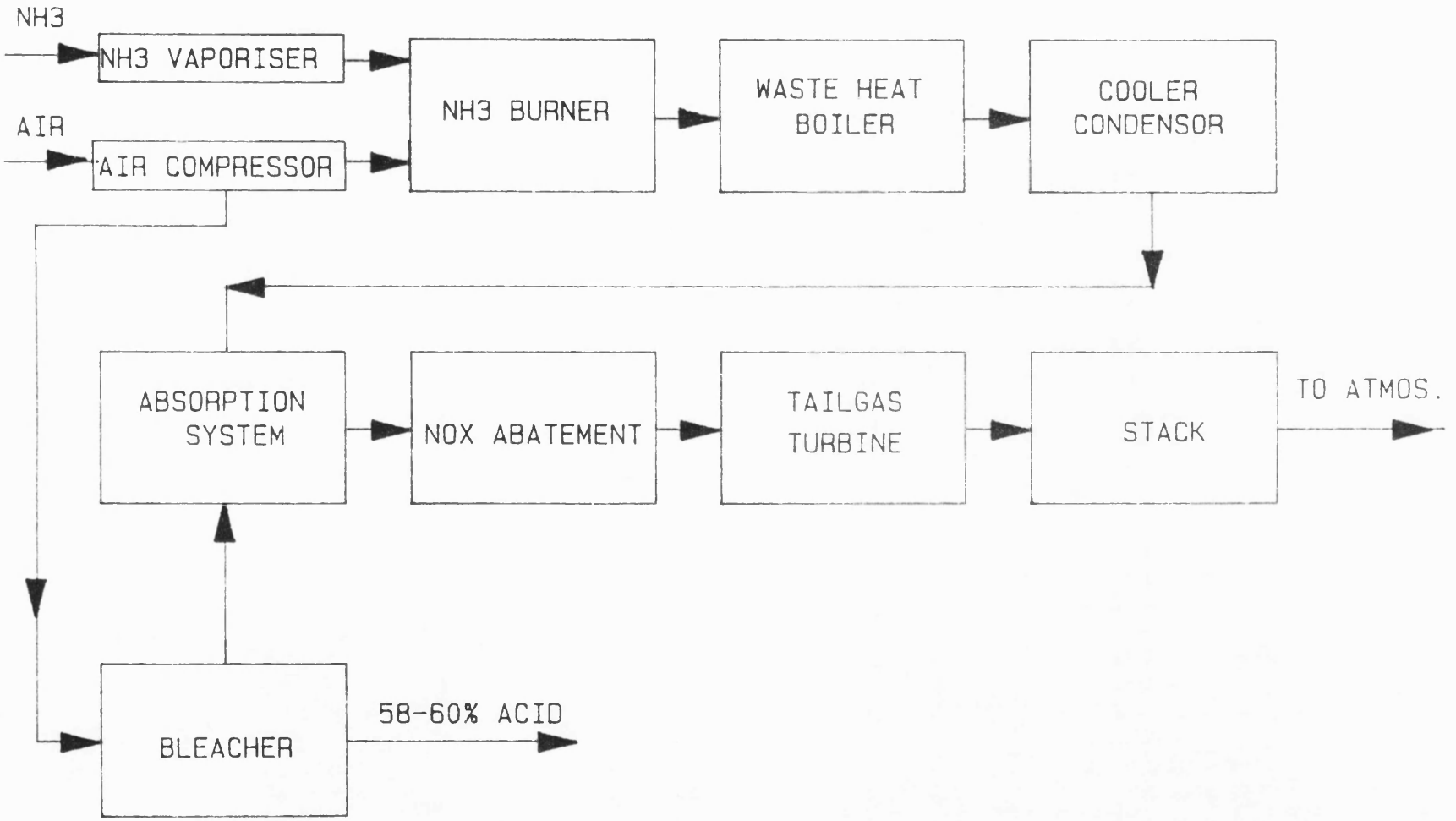


Fig 3.1 Schematic flowsheet of nitric acid plant

The absorption system has a battery of absorption columns. The columns are of the packed bed design in series. Process water is fed into the last packed bed, and the effluent acid from the system is around 59-60% W/W in concentration.

Tailgas from the final absorption tower is reheated in the tailgas heater and fed into the catalytic NOX abatement system, where the concentration of the nitrogen oxides is brought down to 200 ppm (by volume).

Gas from the NOX abatement system is expanded in the tailgas expander which is a part of the air compressor drive train and finally released to the atmosphere via a tall stack.

3.2 Description of the nitric acid process units

The following major equipment are in the nitric acid plant :

1. Air compressor
2. Ammonia vaporiser and superheater
3. Tail-gas heater
4. Ammonia-air Mixer
5. Oxidation Converter
6. Waste heat boiler
7. Cooler-condenser
8. Absorption system
9. Tail-gas expander

3.2.1 Air compressor

The air compressor is an eight-stage axial machine. The drive train consists of a motor, tail-gas expander and a gear-box. As it is a fixed speed machine the capacity-control is achieved by diverting some of the air to the tail-gas expander via a bypass line.

3.2.2 Ammonia vaporiser and superheater

The ammonia vaporiser is a vertically oriented shell-and-tube heat exchanger with boiling ammonia on the shell-side and steam condensate on the tube-side. The superheater consists of a shell and-tube-heat exchanger using condensing steam for superheating the ammonia to prevent the entrainment of liquid ammonia droplets into the gas mixer.

3.2.3 Tail-gas heater

Hot compressed air from the discharge stream of the compressor is used to heat the tail-gas from the absorption system before it is expanded in the tail-gas expander for power recovery. The tail-gas heater consists of a shell-and-tube exchanger with air on the shell-side and tailgas on the tube-side.

3.2.4 Gas mixer

Ammonia from the ammonia superheater and air from the tail-gas heater are mixed in the gas mixer and then fed to the oxidation converter. The mixer is like a modified heat exchanger in which air is introduced on the shell-side and ammonia on the tube-side. The modification consists of the replacement of the

lower tube plate by a plate in which holes are drilled concentric with each tube but with a larger diameter than the diameter of tube. This leads to a turbulent region at the bottom end of each tube, where mixing takes place.

3.2.5 Oxidation Converter

Mixed gas is fed into the top cone of the converter and flows downwards through six layers of platinum-rhodium catalyst gauzes. The catalyst together with the platinum recovery gauzes are supported on randomly dumped raschig rings which promote even flow over the entire area of the catalyst. The bed of raschig rings is itself supported on a grid.

3.2.6 Waste heat boiler

The waste heat boiler is a pressure vessel where the hot process gas leaving the oxidation converter is cooled. It consists of four sections:

The first section is the radiant vaporiser where radiant heat is recovered by circulating water in a close pitched helical coil which acts as a cooling water-wall. The radiant heat comes from two sources. The first source is from the the bed of raschig ring which supports the platinum gauze. At steady state the bed attains a temperature which is only marginally below the temperature of the gas leaving the gauze. The second source of radiant heat is the non-luminous radiation from the gas due to the presence of water vapour produced by the ammonia oxidation reactions. The water-steam mixture which is produced in the helical coil is fed into the steam drum where steam is raised. The radiant vaporiser tubes are piped in parallel with the evaporator. Thus while the

process gas is cooled, the "water wall" absorbs the radiant heat and protects the pressure vessel.

The second section of the WHB consists of the superheater tube bank where steam from the boiler drum is superheated to 315° C prior to export from the plant.

The third section is the evaporator tube bank where water from the steam drum is circulated by circulation pumps. The steam-water mixture that is produced has a dryness fraction of 15-20 % W/W and is piped to the steam drum where steam is raised.

The fourth section is the economiser tube bank where deaerated water from the deaerator is preheated before it is fed into the the steam drum.

3.2.7 Cooler-condenser

The cooler-condenser consists of two heat exchangers: the boiler feed water preheater and the gas cooler.

In the boiler feed water preheater the process gas which is being cooled passes through its dew-point and starts to condense as nitric acid. Severe corrosion would take place at the interface of the wet and dry portions of the tubes if 18-8 stainless steel is used as the material of construction. Hence titanium tubes have been used to keep the process gas on the tube-side and boiler feed water on the shell-side.

In the gas-cooler the saturated process gas is on the shell-side and the cooling water on the tube-side. The process gas is cooled to a temperature of

40-50°C and a condensate of around 35-40% W/W nitric acid is produced.

3.2.8 The absorption system.

The process gas from the gas-cooler is mixed with the tail-gas from the bleacher and fed to the absorption system. The absorption system consists of 4 towers, each having multiple packed beds. In each bed the acid is recirculated by an acid circulation pump and cooled with cooling water to remove the heat of reaction/dissolution. The acid is cascaded from bed to bed and tower to tower flowing in a counter-current direction to the flow of gas to produce an acid of approximately 60% W/W concentration . Pall rings are used as the packing media. The towers, piping, pumps and coolers are constructed with SS 316 Ti (titanium stabilised).

The product acid is finally "bleached" in the bleacher which is a packed tower. Physically absorbed nitrogen dioxide gives nitric acid a brown colorisation. In order to remove the brown colour nitric acid is "bleached" using secondary air. The air strips the physically absorbed nitrogen dioxide. The secondary air together with the nitrogen dioxide is fed back into the absorption system.

3.2.9 Tail-gas expander

The tail-gas expander is an axial flow machine where energy is recovered from the tail-gas before it is discharged into the atmosphere. It is a component of the air compressor drive train .

3.3 Scope of the simulation.

After examining the instrumentation available by studying the P & I diagrams for the nitric acid plant and considering the extent of process information being acquired by the on-line database it was decided to implement the proposed process optimisation on the following process units:

1. Ammonia Oxidation Reactor, hereafter called burner.
2. Waste heat boiler.

Fig. 3.2 shows the process units to be simulated and the various inter-connecting streams. In order to carry out the optimisation of the operation of the above process equipment, the scope of the simulation should include the following items.

1. Air compressor.
2. Mixer.
3. Burner.
4. Waste heat boiler.

3.4 Choice of simulation program.

For the simulation of the nitric acid process, there are two broad possibilities. The first is to use a commerically available flowsheeting package, for example FLOWPACK, PROCESS, FLOWTRAN, ASPEN etc. The second option is to develop a "custom-built" simulator. It must be stressed that either

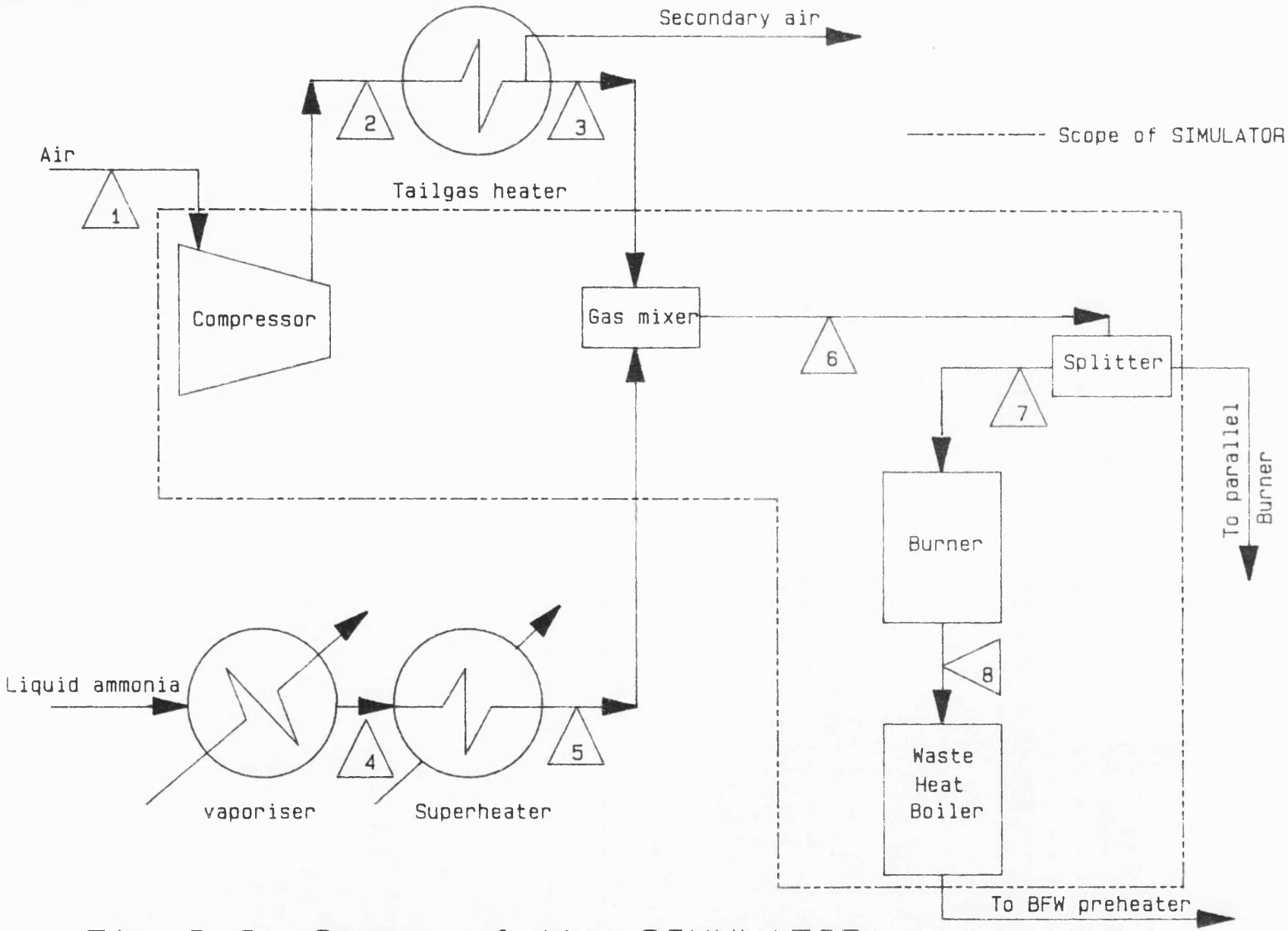


Fig 3.2 Scope of the SIMULATOR

choice does not affect the methodology of optimisation, so long as the fidelity of the simulator is good. In the subsequent section the desirable aspects of a simulation package are discussed.

3.4.1 Desirable features

A number of features must be considered in the selection of the most suitable simulation package. They are:

FEATURE A : Provision to add user written modules for process units.

Most commercially available packages use simple models for units such as reactors, absorption columns, heat exchangers etc. The reactor models are normally of the fixed stoichiometric type, where for example, the conversion in a reactor is a fixed value provided by the user before the execution of the program. Furthermore, only a few packages have a provision to add on user-written modules for process units where mass transfer, heat transfer or kinetics have to be modelled to predict the process performance.

FEATURE B : Flexibility in input and output of data.

A high degree of flexibility in data input and output is desired. This will affect the ease of transfer of data from and to the SIMULATOR, AUDSIM and OPTIMISER.

FEATURE C : A comprehensive physical properties database.

The physical properties database or prediction package must be comprehensive and reliable. Many commercial simulation packages have databases and prediction routines which are biased or devoted to the

hydrocarbon or gas processing industries. Few packages have provision for predicting the thermodynamic or transport properties of acids/salts in aqueous solution. Moreover the equations of state used in many simulation packages may not be suitable for predicting the thermodynamic properties of polar gases or vapours such as ammonia and water.

FEATURE D : Hardware requirements.

Lastly, the choice and availability of hardware where the simulator can be implemented must also be taken into account.

Four simulation packages were considered and their features are listed in the following table.

Feature	A	B	C	D
FLOWPACK II	Yes	Poor	Limited	Mainframe
PROCESS	Yes	Good	Satisfactory	Mainframe IBM PC/AT 370
UNICORN	No	Satisfactory	Poor	Mainframe
CHEMCAD	Yes	Good	Satisfactory	IBM PC/XT
HYSIM	No	Poor	Limited	IBM PC/XT

Table 3.1 Commercial simulation packages considered

3.4.2 Reasons for the choice of Simulator.

After considering the relative merits and drawbacks of the various commercial flowsheet packages available at site it was decided that for the

simulation task it would be more appropriate to develop a customised simulation package. The reasons are as follows:

(i) The simulation of the oxidation reactor. The conversion of ammonia to nitric oxide is very sensitive to the strength of ammonia in the feed, the ammonia rate and its preheat temperature. Clearly a simple stoichiometric reactor model will not be able to simulate the ammonia oxidation process.

(ii) The waste heat boiler. The process gas from the gauzes has to be cooled prior to absorption from 850 to 230 C. As the process gas is cooled it reaches a certain temperature T_{COM} at which the oxidation of nitric oxide to nitrogen dioxide commences. The amount of nitrogen dioxide generated depends on the residence time of the process gas in the equipment after it has been cooled to the initiation temperature T_{COM}. It is very important to account for this conversion of nitric oxide to nitrogen dioxide as a substantial amount of heat is generated, thus adding to the cooling duty of the boiler. None of the packages considered provides an easy means of carrying out the analysis of simultaneous heat transfer and reaction kinetics processes taking place in the waste heat boiler.

(iii) None of the above packages has a comphrensive physical properties database for all the gaseous components present to predict all the physical properties required by the simulation.

(iv) Site conditions and hardware restraints necessitated the implementation of the simulator on an IBM PC-XT and thus limiting the choice of the simulator to HYSIM and Chemcad, neither of which was suitable for the proposed task.

It was concluded that although models and methods for predicting physical properties can be added to some of the above packages it is far more straight forward and efficient to develop a customised simulator in this case.

3.4.3 The architecture of the SIMULATOR

A sequential modular structure has been used for simulating the flowsheet. As the flowheet is simple and no recycle stream is present, iterative calculations are not required for obtaining the simulation results.

The SIMULATOR is made up of the following components:

1. Main executive program.
2. Process unit modules.
3. Physical properties prediction package.

The main executive program controls the execution of the various functions of the SIMULATOR, such as data input and output, calculation of performance using unit modules, providing physical properties of gases or acid solutions when required by the simulation algorithms. In addition, the main executive program also determines the order of the execution of various equipment modules and transfer of process information between them.

The unit modules consist of the algorithms for calculating the performance of the various major process units listed in 3.3. The structure of a module is divided into input, calculation algorithm and output. These modules are based on steady state material and energy balances and the rate processes of the various units.

The physical properties prediction package contains a group of subroutines for predicting thermophysical and transport properties of gases and gas mixtures required for the calculation of the individual unit modules.

3.4.4 Choice of computing language

Shammas (Shammas, 1983.) reviewed three general purpose languages which are suitable for engineering computations on personal computers. These languages are FORTRAN, BASIC and Pascal. He concluded that while BASIC is adequate for most engineering calculations, it is not well suited for data-handling and fast calculation. FORTRAN has the advantage of being more powerful and many existing engineering and mathematical programs are written using FORTRAN. Pascal seems to be most suitable for interrelated design and calculation programs since sub-routines and user functions can be stored and used readily. Pascal requires systematic and structured programming while BASIC and FORTRAN can tolerate "casual" programming.

Neither FORTRAN nor Pascal were available for use on the IBM/XT personal computer at site. Therefore the source codes of the SIMULATOR and OPTIMISER have been written in BASIC. The source code for the SIMULATOR is presented in Appendix 1.

3.5 Input and output options

The SIMULATOR can be run as a part of the entire optimisation procedure or as a stand-alone program to answer the "what ifs" of the nitric acid process analysis. This feature leads to the various input and output options which

are dicussed in the subsequent sections.

The important input variables required for the running of the SIMULATOR are:

1. Primary air flowrate.
2. Ammonia flowrate.
3. Compressor suction pressure.
4. Compressor suction temperature.
5. Compressor discharge pressure.
6. Mixed gas temperature.

These inputs can be supplied directly from the AUDITOR after validation using AUDSIM software which will be discussed later in Chapter 4. The other option is for the user to supply the inputs.

When the SIMULATOR is run it generates the following information.

(i) Calculates and reports the temperature, pressure, composition, enthalpy, and flowrate of the various main process streams.

(ii) Calculates and reports the performance of the major equipment.

When the simulator is run as a part of the optimisation software, it automatically transfers sufficient information required by the information validation and optimisation modules.

On the other hand, when the SIMULATOR is run as a stand-alone program for exploratory process analysis or for trouble shooting purposes the SIMULATOR will report the results of material and heat balances of all streams and performance of the major units.

3.6 The Physical Properties Package

The physical properties package is a vital component of the SIMULATOR, as it provides the various thermophysical and transport properties required to perform heat balances and heat transfer and other process calculations.

3.6.1 The Components

The gases and vapours covered by the physical properties package are:

Component 1: Nitrogen.

Component 2: Oxygen.

Component 3: Ammonia.

Component 4: Water.

Component 5: Nitric Oxide.

Component 6: Nitrogen Dioxide.

3.6.2 Choice of Equation of State (EOS)

As there are several iterative calculations where temperature and enthalpies are estimated, especially in the simulation of the waste heat boiler, it is prudent to use one of the "simple equations of state" for the calculation of compressibilty and enthalpy departure. A "simple equation of state" is taken as an equation in a cubic form in terms of molar volume or compressibility that has two or three adjustable parameters (Edminster and Lee, 1984). Tarakad et al. compared the ability of the following eight equations of state to predict the gas phase density and fugacity (Tarakad, et al., 1979.).

(i) Redlich Kwong (RK), (Redlich and Kwong, 1949)

(ii) Chueh's modification of RK equation (RKC), (Chueh and Prausnitz, 1965).

(iii) Barner-Adler's modification of the Joffe Equation (JBA) (Barner and Adler, 1970).

(iv) Soave's modification of RK equation (RKS) (Soave, 1972).

(v) Virial equation

(vi) Nakamura-Breedveld-Prausnitz (NBP) equation (Nakamura et. al., 1976).

(vii) deSantis, Breedveld and Prausnitz's modification of RK equation (RKD) (deSantis, 1974)

(viii) Guerreri and Prausnitz's modification of RK equation (RKG) (Guerreri and Prausnitz, 1973)

By comparing the calculated values of gas phase density and fugacities using the various equations of state with experimental values, the suitability of the equations for different systems with various combinations of polar and non polar components was studied. From the list of components given in 3.6.1 it can be seen that there are two polar components, water and ammonia. However a study of the process indicates that ammonia appears as the lone polar component in the feed stream to the burner and water vapour is similarly the only polar component

in the gas mixture after the burner. For mixtures containing only one polar component, either the Redlich-Kwong or Virial equation of state is recommended for use in predicting the compressibility factors and fugacities of gaseous mixtures. The RK equation of state was selected out of the two options because it is a "simple" EOS that lends itself to relatively easier computation of the enthalpy departures etc.

3.6.3 Thermophysical and tranport properties prediction

The following thermophysical and transport properties are predicted for the above gases and their mixtures:

1. Compressibility factor and specific volume.
2. Ideal gas enthalpy.
3. Enthalpy departure function.
4. Ideal gas heat capacity.
5. Heat capacity departure function.
6. Ideal gas viscosity.
7. Pressure correction for viscosity.
8. Ideal gas thermal conductivity.
9. Pressure correction for thermal conductivity.

The physical properties package completes the following calculations:

1. Mole fraction, $X_{s,n}$, of the various components found in the gas stream in question are estimated by the equation:

$$X_{s,n} = M_{s,n}/MT_s \qquad .....(3.1)$$

Where $M_{s,n}$ and MT_s are the molar flowrate of component "n" in stream "s" and total molar flowrate of stream "s".

2. Average molecular weight, MW_s is estimated by the equation :

$$MW_s = \sum_n (MW_n.X_{s,n}) \qquad .....(3.2)$$

3. Compressibility factor, z, is estimated using the Redlich-Kwong (Redlich and Kwong, 1949.) equation of state, given below.

$$P = \frac{RT}{(v-b)} - \frac{a}{T^{0.5}v(v-b)} \qquad .....(3.3)$$

where

$$a = 0.42748R^2T_c^2.5/P_c \qquad .....(3.4)$$

$$b = 0.08664RT_c/P_c \qquad .....(3.5)$$

Equation 3.3 can be rearranged to give

$$z^3 - z^2 + BP((A^2/B) - BP - 1)z - (A^2/B).(BP)^2 = 0 \qquad .....(3.6)$$

where

$$A^2/B = a/bRT^{1.5} \qquad .....(3.7)$$

$$B = b/RT \qquad .....(3.8)$$

Equation (3.6) is solved for z, the gas compressibility factor, using the Newton-Raphson method and an initial guess of 1. The specific volume, v, is estimated by

$$v = zRT/P \qquad .....(3.9)$$

4. The estimation of ideal gas enthalpy (with respect to the base enthalpy at 273 deg K), is carried out using the polynomial

$$H^o = A_1 T + B_1 \frac{T^2}{2} + C_1 \frac{T^3}{3} + D_1 \frac{T^4}{4} \qquad \text{.....(3.10)}$$

The polynomial coefficients are available in the literature (Reid et al., 1977)

5. Enthalpy departure (pressure correction). The enthalpy departure, H-H°, is calculated based on the RK equation of state (Edminster and Lee, 1984).

$$H - H^o = Pv - RT - 1.5A/(BT).\ln((V+B)/V) \qquad \text{.....(3.11)}$$

6. The ideal gas heat capacity at constant pressure is estimated from the polynomial below.

$$C_p = A_1 + B_1 T + C_1 T^2 + D_1 T^3 \qquad \text{.....(3.12)}$$

7. The heat capacity departure (pressure correction) is calculated by the equation.

$$C_p - C_p^o = 0.75 K_1 \mathrm{Ln}(1+h) + \frac{0.5 K_1 h \frac{(1-h)}{(1+h)}(0.25 K_1 h - (2-h))}{\frac{(1+h)}{(1-h)} - K_1 h \frac{(1-h)}{(1+h)}} \qquad \text{.....(3.13)}$$

where $K_1 = A^2/B$ and $h = b/v$

8. The ideal gas viscosity is estimated for each component by the polynomial.

$$\mu_{s,n} = A_2 + B_2 T + C_2 T^2 \qquad \text{.....(3.14)}$$

9. The ideal gas viscosity for the mixture is estimated from the individual viscosities of the components (Holland et al., 1970).

$$\mu_s^0 = \frac{\sum_n X_{s,n} \mu_{s,n} MW_n^{0.5}}{\sum_n X_{s,n} MW_n^{0.5}} \qquad \text{.....(3.15)}$$

10. The pressure correction for viscosity of the mixture is calculated using the Dean and Stiel method (Dean and Stiel, 1965).

$$\mu_s = \mu_{s,n} + \frac{1.08}{\xi_m}\{\exp 1.439\rho_{rm} - \exp -1.111\rho_{rm}\} \quad .....(3.16)$$

where

$$\rho_{cm} = P_{cm}/(z_{cm}RT_{cm}) \quad .....(3.17)$$

$$\rho_{rm} = \rho_m/\rho_{cm} \quad .....(3.18)$$

$$\xi_m = T_{cm}/(P_{cm}^{2/3}MW_s^{1/2}) \quad .....(3.19)$$

Dean and Stiel used the modified mixing rules of Prausnitz and Gunn (Reid et al., 1973) for calculating the psuedocritical constants, given by the following equations:

$$T_{cm} = X_{s,n}T_{c(n)} \quad .....(3.20)$$

$$z_{cm} = X_{s,n}z_{c(n)} \quad .....(3.21)$$

$$v_{cm} = X_{s,n}v_{c(n)} \quad .....(3.22)$$

$$P_{cm} = X_{s,n}P_{c(n)} \quad .....(3.23)$$

11. Ideal gas thermal conductivity is estimated for each component of the mixture by the polynomial

$$k_{s,n} = A_3 + B_3T + C_3T^2 + D_3T^3 \quad .....(3.24)$$

12. The ideal gas thermal conductivity for a mixture of N species can be calculated by the equation (Holland, 1970):

$$k_s^o = \frac{\sum_n X_{s,n}k_{s,n}MW_n^{1/3}}{\sum_n X_{s,n}MW_n^{1/3}} \quad .....(3.25)$$

13. Pressure correction for thermal conductivity is arrived at using the Stiel and Thodos method (Stiel and Thodos, 1964) :

For $\rho_{rm} < 0.5$

$$k_s = k_s^o + \left(\frac{14E-08}{\Gamma z_c^5}\right)\{\exp(0.535\rho_{rm}) - 1\} \quad \ldots.(3.25)$$

For $0.5 < \rho_{rm} < 2.0$

$$k_s = k_s^o + \left(\frac{13.1E-08}{\Gamma z_c^5}\right)\{\exp(0.67\rho_{rm}) - 1.069\} \quad \ldots.(3.26)$$

For $2.0 < \rho_{rm} < 2.8$

$$k_s = k_s^o + \left(\frac{2.976E-08}{\Gamma z_c^5}\right)\{\exp(1.155\rho_{rm}) - 1\} \quad \ldots.(3.27)$$

3.7 The Air compressor module

The inlet stream is atmospheric air and the outlet stream is compressed air which is fed into the tail-gas heater, where the tail-gas is preheated prior to NO_x abatement. The stream numbers are:

Inlet Stream Number : 1 (air)

Outlet Stream Number : 2 (Compressed air)

The input variables for this module are :

1. Suction pressure, P(1).

2. Suction temperature, T(1).

3. Volumetric flowrate, V(1)

4. Mole fractions.

5. Discharge pressure, P(2).

The calculated output variables for this module are :

1. Discharge temperature, T(2).

2. Enthalpy of compressed air, H(2).

2. Power consumed at the shaft.

The simulation of the air compressor is done according to the following steps:

1. The compressibility factor at the suction side of the compressor (Stream Number 1) is calculated using the physical properties package.

2. The polytropic exponent, n, using a k value, i.e., Cp/Cv, (for air = 1.4) and a polytropic efficiency of 85% (McKetta, 1979) for the axial compressor is given by

$$\frac{n}{(n-1)} = \frac{0.85k}{(k-1)} \qquad \text{.....(3.28)}$$

3. The compressor discharge temperature is calculated by the equation below

$$T_2 = T_1(P_2/P_1)^{(n-1)/n} \qquad \text{.....(3.29)}$$

4. The compressibility factor at discharge can be calculated as the discharge temperature and pressure are known.

5. The average compressibility, z_a, of the compressibilities at inlet and outlet conditions, is calculated and the shaft power estimated by equation 3.30.

$$sp = z_a T_1 R \frac{n}{(n-1)} \left\{ \left(\frac{P_2}{P_1} \right)^{\frac{(n-1)}{n}} - 1 \right\} \qquad \text{.....(3.30)}$$

3.8 The Gas mixer Module

The inlet streams are air from the tail-gas heater and ammonia from the the ammonia superheater. The mixed gas is fed to the burner.

Inlet stream numbers : 3 (air)

5 (ammonia)

Outlet stream number : 6 (mixed gas)

The inputs to this module are:

1. Molar flowrates of incoming streams

   of air and ammonia, MT(3) and MT(5).

2. Temperatures of the incoming streams

   T(3) and T(5).

3. Pressure, P(5).

The calculated outputs from this module are :

1. Outlet molar flowrate, MT(6).

2. Outlet mole fractions.

3. Outlet temperature, T(6).

4. Outlet enthalpy H(6).

The algorithm for calculating the outputs are:

1. The sum of the molar flowrates and enthalpies of the two incoming streams, i.e. air and ammonia, yields the molar flow rate and enthalpy of the outlet stream respectively.

$$MT_6 = MT_3 + MT_5 \qquad \text{.....(3.31)}$$

$$H_6 = \left(A_1 T_6 + B_1 \frac{T_6^2}{2} + C_1 \frac{T_6^3}{3} + D_1 \frac{T_6^4}{4} \right) + (H - H^o) = H_3 + H_5 \qquad \text{.....(3.32)}$$

where H-H° is the enthalpy departure for the gas mixture at the temperature and pressure of stream 6.

2. Using the enthalpy module of the physical properties package and the Newton-Raphson iterative procedure equation 3.32 is solved for the outlet temperature of the mixed gas (stream 6). The derivative was found by analytically differentiating equation 3.32. The tolerance limit for convergence was set at 0.5%.

3.9 The Burner Module

The inlet stream consists of an ammonia air mixture coming from the gas mixer. The outlet stream is converted containing nitric oxide, nitrogen, oxygen and water vapour.

Inlet stream number : 7 (mixed gas)

Outlet stream number : 8 (converted gas)

The inputs to this module are :

1. Molar flowrate, MT(7)

2. Mole fractions.

3. Temperature of the incoming stream, T(7).

4. Pressure of operation, P(7)

The calculated outputs for this module are:

1. The ammonia conversion efficiency of the burner.

2. The molar flowrate, MT(8),

3. Mole fractions.

4. The outlet temperature, T(8).

5. The outlet enthalpy, H(8).

At the heart of the nitric acid process is the burner where ammonia is

converted to nitric oxide over a platinum gauze catalyst by the following reaction:

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad \text{.....(3.33)}$$

There are other side reactions taking place by which ammonia is degraded to nitrogen. These "loss-making" reactions are:

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O \quad \text{.....(3.34)}$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \quad \text{.....(3.35)}$$

$$4NH_3 + 6NO = 5N_2 + 6H_2O \quad \text{.....(3.36)}$$

$$2NO = N_2 + O_2 \quad \text{.....(3.37)}$$

$$2NH_3 = N_2 + 3H_2 \quad \text{.....(3.38)}$$

Heck et al. studied nitrous oxide formation by reaction 3.34 during the oxidation of ammonia (Heck et al., 1982). Pignet and Schmidt published emperical data on the rate of total nitrogen produced by the reactions 3.34 through 3.38 (Pignet and Schmidt, 1975).

In addition to the above "loss-making" reactions there are more side reactions that could take place in the gas phase.

$$4NH_3 + 6NO = 5N_2 + 6H_2O \quad \text{.....(3.39)}$$

$$2NO = N_2 + O_2 \quad \text{.....(3.40)}$$

Wise and French studied and published data on the reaction rate of reaction 3.39 (Wise and French, 1954). Using the data of Ermenc it was seen that the rate of reaction 3.40 was very low at the temperature of operation of the burner and had negligible effect on the burner model if ignored (Ermenc, 1956).

The primary objective in the design of the burner is to maximise the

conversion of ammonia to nitric oxide. The fraction of the ammonia feed that is converted to nitric oxide is called the ammonia efficiency of the burner. With a careful design of the burner it is possible to achieve around 92-96 % ammonia efficiency.

The rate determining step for Reaction 3.33 has been found to be the mass transport of ammonia to the catalyst surface (Andrussow, 1926 and 1927). It has also been reported that higher temperatures of operation increase the ammonia efficiency. However the loss of platinum increases dramatically at temperatures above 915 C which is the upper temperature limit of the burner.

Based on Andrussow's study the rate of oxidation of ammonia to nitric oxide can be expressed in terms of the rate of mass transfer, r_{NH3} of ammonia to the catalyst surface.

$$-r_{NH3} = k_g A (p_{bulk} - p_{cat}) \qquad .....(3.41)$$

where kg is the mass transfer coefficient, A is the surface area of the gauze, p_{bulk} and p_{cat} are the partial pressures of ammonia in the bulk gas and the catalyst surface respectively.

Because of the high flow rate the effect of axial diffusion can be ignored and a plug flow reactor assumed (Rase, 1968). The reactor is modelled by the plug-flow reactor equation:

$$-\frac{F}{M_F} dy_{NH3} = -r_{NH3} dz \qquad .....(3.42)$$

Since the conversion of ammonia to nitric oxide is very rapid with a reaction time in the order of 10^{-11} seconds, the concentration of ammonia on the

catalyst surface is assumed to be zero. The rate of transfer of ammonia to the catalyst surface over a differential bed depth, dz, can be represented by the following equation:

$$-r_{NH3}dz = k_g A\, y_{NH3} P\, dz \qquad .....(3.43)$$

where y_{NH3} and P are the ammonia mole fraction in the bulk and burner operating pressure respectively.

Equation 3.43 can be rewritten in terms of the number of gauzes, n_s and the catalytic surface area of one gauze per unit cross-sectional area, A_g of the reactor.

$$-r_{NH3}dz = k_g A_g y_{NH3} P\, dn_s \qquad .....(3.44)$$

Combining equations 3.42 and 3.44 we can write the equation:

$$-\frac{F}{M_F} dy_{NH3} = k_g A_g y_{NH3} P\, dn_s \qquad .....(3.45)$$

Making an assumption that there is constant molar flow across the burner equation 3.45 is integated to yield an expression for the conversion of ammonia at the outlet of the platinum gauze pack.

$$k_g A_g P\, n_s = \frac{F}{M_F} \ln \frac{y_{NH3}}{y_{NH3_{out}}} \qquad .....(3.46)$$

Rewriting equation 3.46 in terms of ammonia conversion to nitric oxide, X_{NH3}, yields an equation to estimate the conversion of ammonia :

$$X_{NH3} = 1 - e^{\left(-k_g P\, n_s A_g M_F / F\right)} \qquad .....(3.47)$$

The mass transfer coefficient, k_g can be calculated from J_D which can be estimated using the Satterfield and Cortez correlation (Satterfield and Cortez,

1970). The Reynolds number is based on the wire diameter and interstitial velocity while the Stanton number is also based on the interstitial velocity.

$$J_D = 0.865 N_{Re}^{-0.648} \pm 12.5\% \qquad .....(3.48)$$

where $J_D = N_{St} N_{Sc}^{2/3}$ and $N_{Re} = dG_i/\mu$ .....(3.49)

Micrographs of the platinum gauze that have been in service show a rearrangement in the surface with the initial smooth surface turning into one having a "cauliflower" like growth thus increasing the platinum wire diameter (Connor,1967). The increase in wire diameter will increase the J_D factor. This is confirmed by the observation that there is an increase in ammonia efficiency after the new gauzes have been in service for approximately a week. Any model which predicts the efficiency of the burner with good accuracy will have to consider the enhancement in the J_D factor due to surface rearrangement of the platinum gauze.

Using proprietory data on "loss-making" reactions from operating nitric acid plants and published literature and combining with the present method for calculating ammonia efficiency of the reaction 3.33 (nitric oxide formation) a rigorous model was produced to predict the overall efficiency of the burner to within 0.5 % accuracy.

Using the rigorous model described above a paramateric model for correlating the ammonia efficiency of the burner with ammonia flow rate, ammonia concentration and feed gas temperature was developed. The parameteric model that has been incorporated into the SIMULATOR is only applicable to the particular nitric acid plants being modelled. This is because the

parameteric model is based on the results generated by the rigorous model using design variables such as gauze diameter, number of gauzes etc. which are relevant to the particular nitric acid plant.

3.10 The waste heat boiler

The inlet streams into the waste heat boiler (WHB) are converted gas from the burner and boiler feed water. The outlet streams are cooled converted gas and superheated steam.

Inlet stream numbers : 8 (converted gas)

: 12 (feedwater)

Outlet stream numbers : 9 (converted gas)

: 13 (superheated steam)

The input variables to this module are:

1. Molar flowrate, composition, temperature, pressure and enthalpy of the converted gas at WHB inlet.
2. Temperature and pressure of the boiler feed water.

The calculated outputs from this module are:

1. Molar flowrate, composition, temperature and enthalpy of the converted gas at WHB outlet.
2. Superheated steam temperature.

A schematic diagram of the waste heat boiler (WHB) is shown in Fig. 3.3. The converted gas from the gauze enters the radiant evaporator section of the WHB, where it flows past a close pitched coil water wall. Vaporising water flows through the inside of the coil. The gas then flows through a superheater bundle, an evaporator tube bundle and lastly through an economiser tube bundle.

Water is fed into the economiser and then piped into the steam drum. By means of circulation pumps water is circulated through the evaporator and radiant coil producing a water-steam mixture which is returned to the drum. Saturated steam is sent to the superheater, where it is superheated and exported from the plant.

3.10.1 Oxidation reactions and their kinetics

The nitric oxide that is formed has to be oxidised to higher oxides before it can be absorbed to form nitric acid. As the temperature is reduced nitrogen dioxide is formed. This is a time-dependent step. Dinitrogen tetraoxide is formed by the dimerisation of nitrogen dioxide. Nitrogen trioxide is formed by the reaction between nitrogen dioxide and nitric oxide.

The oxidation reactions can be represented by the following equations.

$$2NO + O_2 = 2NO_2 \qquad \Delta H = -57.1 kJ/mol \qquad .....(3.50)$$

$$2NO = N_2O_4 \qquad \Delta H = -28.62 kJ/mol \qquad .....(3.51)$$

$$NO + NO_2 = N_2O_3 \qquad \Delta H = -40 kJ/mol \qquad .....(3.52)$$

The equilibrium constant, reaction rate constant and thus the reaction rate for reactions 3.31 and 3.32 can be calculated by the equations in Table 3.1.

Reaction Number	Equilibrium Constant	Reaction Rate Constant
3.50	$Ln(K_p)=5914/T-7.513$	$Ln(k_p)=652.1/T$ -1.0366
3.51	$Ln(K_p)=2993/T-9.226$	10^4 times the values of constant for Reaction 3.50.

Table 3.1 Equilibrium and reaction rate constants for oxidation reactions (Emig et al., 1979)

The net forward rate of reaction of the oxidation of nitric oxide by reaction 3.50 can be written in terms of the initial partial pressures, "a" and "b" of NO and O_2 respectively (Solomon, 1963):

$$\frac{dx}{d\Theta}=k_1(a-x)^2\left(b-\frac{x}{2}\right)-k_2x^2 \qquad .....(3.53)$$

x is the fall in NO partial pressure in time, and θ is the residence time,

k_1 is the forward reaction rate constant,

and k_2 is the backward reaction rate constant.

At lower temperatures k_2 approaches zero, while at higher temperatures, the rate constant for the forward reaction is high, and x approaches zero. Hence in either case the term k_2x^2 can be neglected. Integrating and rearranging equation

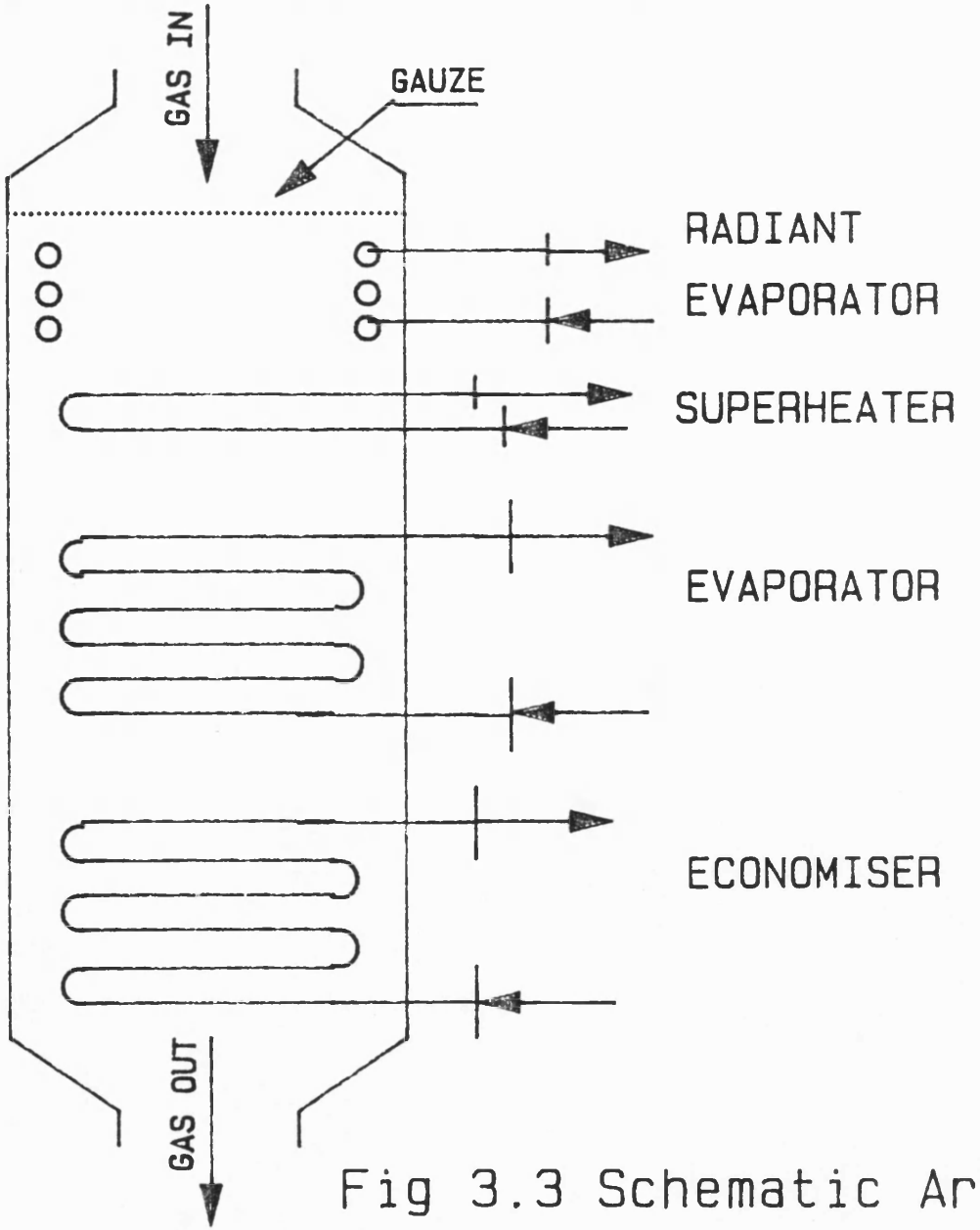


Fig 3.3 Schematic Arrangement of the WHB

3.53 gives

$$\frac{(2b-a)^2}{2}k_1\Theta+\ln\left\{\frac{a}{(a-x)}.\frac{(b-0.5x)}{b}\right\}=(2b-a).\left\{\frac{1}{(a-x)}-\frac{1}{a}\right\} \qquad \ldots.(3.54)$$

The above equation is valid between the upper and lower temperature limits. The upper limit is the point at which the forward rate is equal to the backward rate and the lower limit is the dew point of the process gas. Solomon and Hodges (Solomon and Hodges, 1963) showed that at the upper temperature limit the following equation is valid:

$$K_E=\frac{1}{(a+b)} \qquad \ldots..(3.55)$$

Using equation 3.55 we can now calculate the value of the overall equilibrium constant, K_E, as the initial partial pressures of nitric oxide and oxygen are known. As the process gas is being cooled from the temperature at the burner outlet, it reaches a particular temperature, T_{COM}, at which the formation of nitrogen dioxide initially commences. As the value of K_E is known we can proceed to calculate the temperature of commencement of oxidation, T_{COM} corresponding to K_E from equation 3.55.

3.10.2 The Extent of Oxidation

The conversion of nitrogen dioxide to higher oxides by reactions 3.51 and 3.52 have been estimated and found to be negligible in the temperature range of operation of the WHB. Hence these reactions are neglected in the simulation model. The only oxidation reaction to be considered is therefore the conversion

of nitric oxide to nitrogen dioxide by reaction 3.50.

Fig.3.4 shows a cross-section of the evaporator tube bundle. The economiser tube bundle is similar except for tube dimensions and pitch. The hatched area shows the reaction space where the oxidation of nitric oxide occurs.

For the purpose of calculating conversion, the evaporator and economiser tube bundles can be divided into smaller elements. The size of the elements chosen was one row of tubes. The reaction volume contained in each element was estimated by analysing the detailed engineering drawings of the WHB.

The inlet temperature of each element is estimated by calculating the cooling of process gas in the previous element. The specific volume of gas at the inlet temperature of each element can then be calculated. The residence time, θ, in the element can be calculated assuming plug flow conditions. As the oxidation reaction is a homogenous reaction the assumption of plug flow is reasonable.

$$\Theta = M_F v / V_{El} \qquad \text{.....(3.56)}$$

The extent of oxidation of nitric oxide in each element of the tube bundle, in time, θ, with known initial partial pressures of NO and O_2 can be calculated by equation 3.54. This calculation can be performed for each element.

Using this method, the conversion in all the individual elements and consequently the overall conversion in the WHB are calculated.

3.10.3 The Evaporator and Economiser Heat Load

In estimating the heat load of the WHB, the following procedure is adopted.

As in the case of calculating the extent of oxidation, the WHB is divided

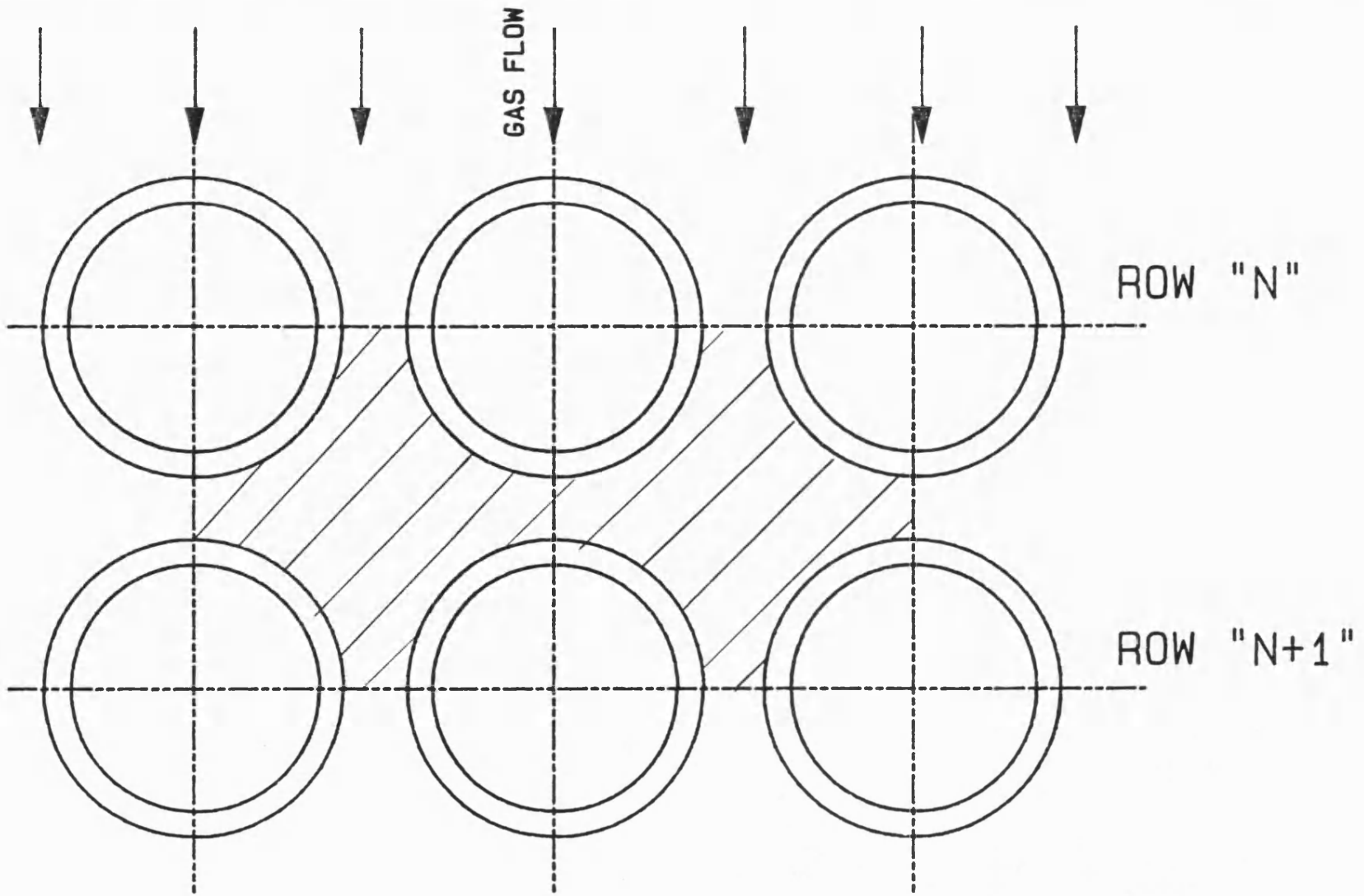


Fig. 3.4 Cross-section of evaporator tube bundle

into a number of elements where each element contained a row of tubes. For each element the sensible heat change of the gas stream is calculated until the element where the temperature T_{COM} is reached. This is done by estimating the overall heat transfer coefficient for each element and then calculating the amount of cooling of the process gas in the element.

From the element where the temperature T_{COM} is reached to the last element of the evaporator or economiser, the conversion of nitric oxide to dioxide, the heat of reaction , and the sensible heat change in the process gas and steam/water mixture are calculated for each element. The heat load of each element is the sum of the sensible heat change of the process gas and the heat of reaction.

The sum of the heat loads of all the elements gives the total heat load of the WHB.

3.10.4 Heat transfer Coefficients

1. The heat transfer coefficient, h_i for flow inside tubes for fully developed turbulent flow is calculated using Dittus-Boelter equation (Janna, 1986) with the fluid properties estimated at the mean bulk temperatures.

$$h_i = 0.023\frac{k}{d_i}Re^{0.8}Pr^{n} \qquad .....(3.56)$$

where n=0.4 for heating and 0.3 for cooling.

The Prandtl number, Pr, range is $0.7 < Pr < 160$.

The Reynolds number, Re, should exceed 10000.

$L/d_i >= 60$.

k= Thermal conductivity.

2. For the calculation of the liquid film heat transfer coefficient, h_{ic}, in a helical coil the following equation is used (McAdams, 1954a).

$$h_{ic} = h_i\left(1 + 3.5\frac{d_i}{d_o}\right) \qquad \text{.....(3.57)}$$

3. For the calculation of the boiling heat transfer coefficient, h_{tp}, inside a helical coil where dryness fractions varies between 0 to 0.7 Chen's correlation (Chen, 1967) was recommended by Butterworth and Shock (Butterworth and Shock, 1982.)

$$h_{tp} = h_{ic}F + h_b S\left(\frac{d_i}{d_o}\right) \qquad \text{.....(3.58)}$$

where h_b is the nucleate boiling heat transfer coefficient calculated using the correlation of Forster and Zuber (Equation 3.59) below.

F is the liquid forced convection coefficient factor due to vapour generation

S is the nucleate boiling suppression factor.

Ganapathy has provided graphs for estimating the values of F and S (Ganapathy, 1985a).

4. For the calculation of the nucleate boiling coefficient, h_b, correlation of Forster and Zuber (Forster and Zuber, 1967) is used.

$$h_b = \Delta T_w^{0.24} \times \Delta P_w^{0.75} \times (\text{ a function of the fluid properties}) \qquad \text{.....(3.59}a\text{)}$$

ΔT_w = Temperature difference between the wall and the boiling fluid temperatures.

ΔP_w = Satuation pressure difference between wall

and boiling fluid temperatures.

Equation 3.59a can be approximated by the following equation for ease of computation (Ganapathy, 1985).

$$h_b = \frac{25.6 k_l^{0.787} Cp_l^{0.453} \rho_l^{0.49} hl_g^{0.51} \rho_g^{0.51} \Delta t_w}{\sigma_g^{0.5} \mu_g^{0.278} (t_{sat} + 4.6)^{0.75}} \qquad \text{.....(3.59}b\text{)}$$

where k_l is the liquid thermal conductivity.

C_{pl} is the liquid heat capacity.

ρ_l is the liquid density.

h_{lg} is the latent heat.

ρ_g is the vapour density

σ_l is the surface tension.

μ_l is the liquid viscosity.

t_{sat} is the saturation temperature.

The constant in equation 3.59b is 25.6 when the variables are in "British Engineering" Units.

5. The calculation of radiant heat transfer coefficient, h_r, is carried out by using the following equation.

$$h_r = \sigma \frac{(\varepsilon T_{gs}^4 - \alpha T_w^4)}{T_{gs} - T_w} \qquad \text{.....(3.60)}$$

where ϵ is the emissivity of the radiating surface at temperature, Tgs, and α_g is the absorptivity of the surface at temperature T_w.

If T_g is much higher than T_w, as is the case in industrial furnaces and reactors the absorptivity is taken to be equal to emissivity. The error introduced by this assumption is negligible.

6. Calculation of the the heat transfer coefficient, h_o, for crossflow over tube bundles is carried out using Grimison's equation (Janna, 1986b).

$$h_o = 1.13 C_1 C_2 \frac{k}{d_o} Re^m Pr^{1/3} \qquad .....(3.61)$$

The constants C_1 and m are functions of the tube spacing while C_2 is a function of of the number of rows. Appropriate values of constants can be selected from the tables supplied by Janna (Janna, 1986).

7. Non-luminous heat transfer coefficient, h_n, can be estimated, using the following procedure:

a. Gases such as carbon dioxide, water vapour, carbon monoxide, hydrocarbons, ammonia, hydrogen chloride and alcohols radiate heat in the infra-red range at operating temperatures of industrial furnaces. Hottel and Mangelsdorf measured the emissivity of carbon dioxide at 1 atm. total pressure and different temperatures and partial pressures of the gas (Hottel and Mangelsdorf, 1935). The radiating gas was considered to be hemispherical in shape, with a radius L, and the radiant heat interchange between the gas and an area of surface located at the centre of the base of the hemishpere was measured. Similar experiments have generated data on the emissivity of other gases such as water vapour, ammonia and sulphur dioxide. "Hottel's charts", Fig. 3.7, are used

to express the emissivity data in terms of gas partial pressure, total pressure, temperature and beam length .

Beam length is a concept used for defining the shape of the radiating gas (which will vary according to the design of heat transfer equipment) in terms of a hemisphere of gas of radius L, which will radiate to unit area at the centre of of its base with the same average radiation as from the actual gas. The radius, L, is the beam length that must be used in the Hottel's chart to evaluate the gas emissivity.

The calculation of the emissivity of the gas is carried out using the gas temperature T_g, the water vapour partial pressure and the beam length, together with Hottel's charts (McAdams, 1954b). Ganapathy presented beam lengths for various furnace configurations (Ganapathy, 1983).

b. Calculation of h_n, using the following equation:

$$h_n = \sigma \varepsilon_g \frac{(T_g^4 - T_w^4)}{(T_g - T_w)} \qquad \text{.....(3.62)}$$

3.10.5 Simulation

The simulation of the WHB can be divided into four parts :

1. Radiant evaporator.
2. Superheater.
3. Evaporator.
4. Economiser.

Radiant Evaporator (RE)

The radiant evaporator is fed with saturated water from the the steam drum of the WHB. As the water flows through the RE, part of it vaporises to produce a water-steam mixture leading to two phase flow conditions.

The method of the simulation model is explained with reference to the flowchart in Fig.3.5.

(i) The first step is to calculate the heat flux, H_i, at the inlet of the RE, where the dryness fraction, X, is equal to 0, as water at its saturation conditions is being fed from the boiler drum. This is done as follows:

(ii) The radiant heat flux based on developed area, i.e., the outer surface area of the tube that is actually exposed to radiant heat, is given by the equation:

$$q_d = h_r(T_g - T_w) + h_n(T_g - T_w) \qquad .....(3.63)$$

where h_r and h_n can be estimated by equations 3.60 and 3.61 respectively.

(iii) The RE receives radiant heat from the gauze support as well as non-luminous radiation from the process gas due to the presence of water vapour.

After calculating the view factor of a tube located at the middle of the helical coil which represents the average view factor of the coil, the maximum radiant flux is found to be 1.2 times the flux based on developed area. On this basis we can write the equation for the flow of radiant heat to the boiling water steam mixture as:

$$h_i \frac{d_o}{d_i}(T_w - T_s) = 1.2\{h_r(T_{gs} - T_w) + h_n(T_g - T_w)\} \qquad .....(3.64)$$

(iv) The next step is the estimation of radiant heat flux, q_p, at the coil inlet where the dryness fraction, X, of the water in the helical coil is equal to zero. As the radiant heat transfer coefficient is a function of T_w, an iterative procedure using Newton-Raphson method is employed for solving Equation 3.64 for T_w. The derivative is given by an algebraic equation which is the result of the differentiation of equation 3.64. The tolerance limit for convergence chosen is 0.1%.

(v) The approximate heat duty, Q, and exit steam quality, X, based on the inlet heat flux is calculated.

$$Q = q_p A_{re}$$

(vi) The heat flux, q_p, at the coil outlet maybe calculated, based on the steam quality calculated in step (v). The approach used in calculating the inlet flux is used here, except that consideration is given to the fact that boiling is taking place inside the tubes. The single phase heat transfer coefficient h_i, in equation 3.64 is replaced by the two phase flow heat transfer coefficient h_{tp}, and is calculated using Chen's correlation (explained in Section 3.10.4) for two phase flow.

(vii) The average heat flux between the inlet and outlet fluxes is calculated. The heat duty, Q, is estimated based on the average heat flux, and the outlet steam quality are recalculated.

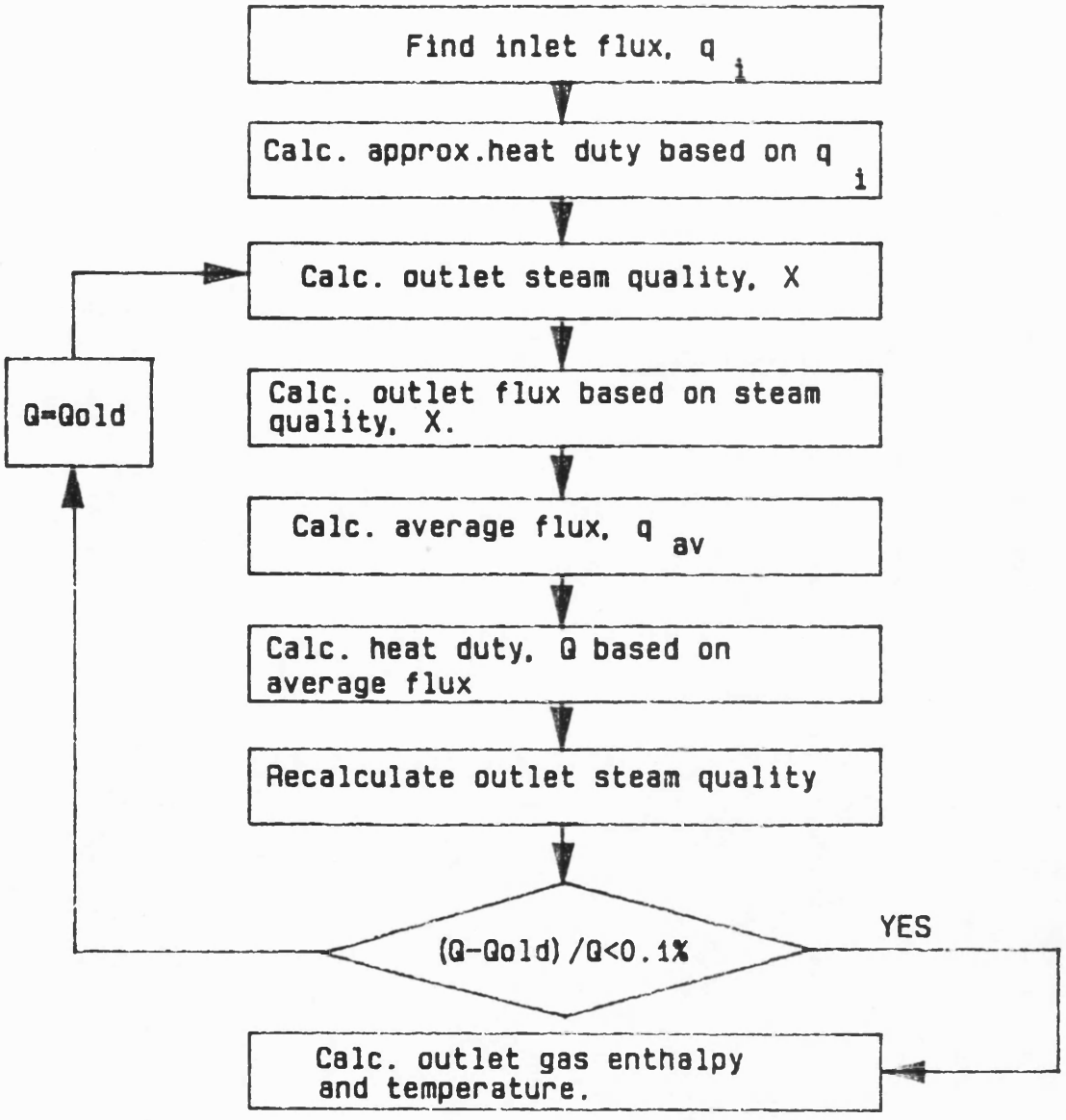


Fig 3.5 Algorithm for radiant evaporator

(iv) The next step is the estimation of radiant heat flux, q_p, at the coil inlet where the dryness fraction, X, of the water in the helical coil is equal to zero. As the radiant heat transfer coefficient is a function of T_w, an iterative procedure using Newton-Raphson method is employed for solving Equation 3.64 for T_w. The derivative is given by an algebraic equation which is the result of the differentiation of equation 3.64. The tolerance limit for convergence chosen is 0.1%.

(v) The approximate heat duty, Q, and exit steam quality, X, based on the inlet heat flux is calculated.

$$Q = q_p A_{re} \qquad \text{.....(3.65)}$$

(vi) The heat flux, q_p, at the coil outlet maybe calculated, based on the steam quality calculated in step (iii). The approach used in calculating the inlet flux is used here, except that consideration is given to the fact that boiling is taking place inside the tubes. The single phase heat transfer coefficient h_i, in equation 3.64 is replaced by the two phase flow heat transfer coefficient h_{tp}, and is calculated using Chen's correlation (explained in Section 3.10.4) for two phase flow.

(vii) The average heat flux between the inlet and outlet fluxes is calculated. The heat duty, Q, is estimated based on the average heat flux, and the outlet steam quality are recalculated.

(viii) Step (vii) is repeated using the heat duty and steam quality recalculated in step (vii) until a specified tolerance limit, say 0.1%, for the accuracy of heat duty is reached.

(ix) Once the heat duty of the RE is known, the process gas temperature at the exit iof the RE is calculated.

Superheater (SH)

The algorithm for simulating the superheater is given in Fig.3.6 and Fig.3.6a.The SH tube bundle is analysed for heat transfer row by row. The steps of the calculation are:

a. The fraction, K_n, of the total radiant heat received by each tube row is calculated using an analytical expression developed from the geometry of the system (Ganapathy, 1982), where N_H is the row number.

$$K_n = 1 - \left\{ \left(\left(1 - \frac{d}{S_T} \right)^2 - \frac{d}{S_T \psi} \right)^{0.5} \right\}^{N_H} \qquad .....(3.65)$$

$$\text{where } \psi = \cos^{-1}\left\{ \frac{d_o}{S_T} \right\} \qquad .....(3.66)$$

b. The following heat balance equation can be written by equating the sum of radiant heat from the gauze support (term 1 of equation 3.67), the convective heat and the non-luminous radiant heat from the gas (term 2 of equation 3.67) with the heat removed by steam flowing inside the tubes (the right hand-side term of Equation 3.67).

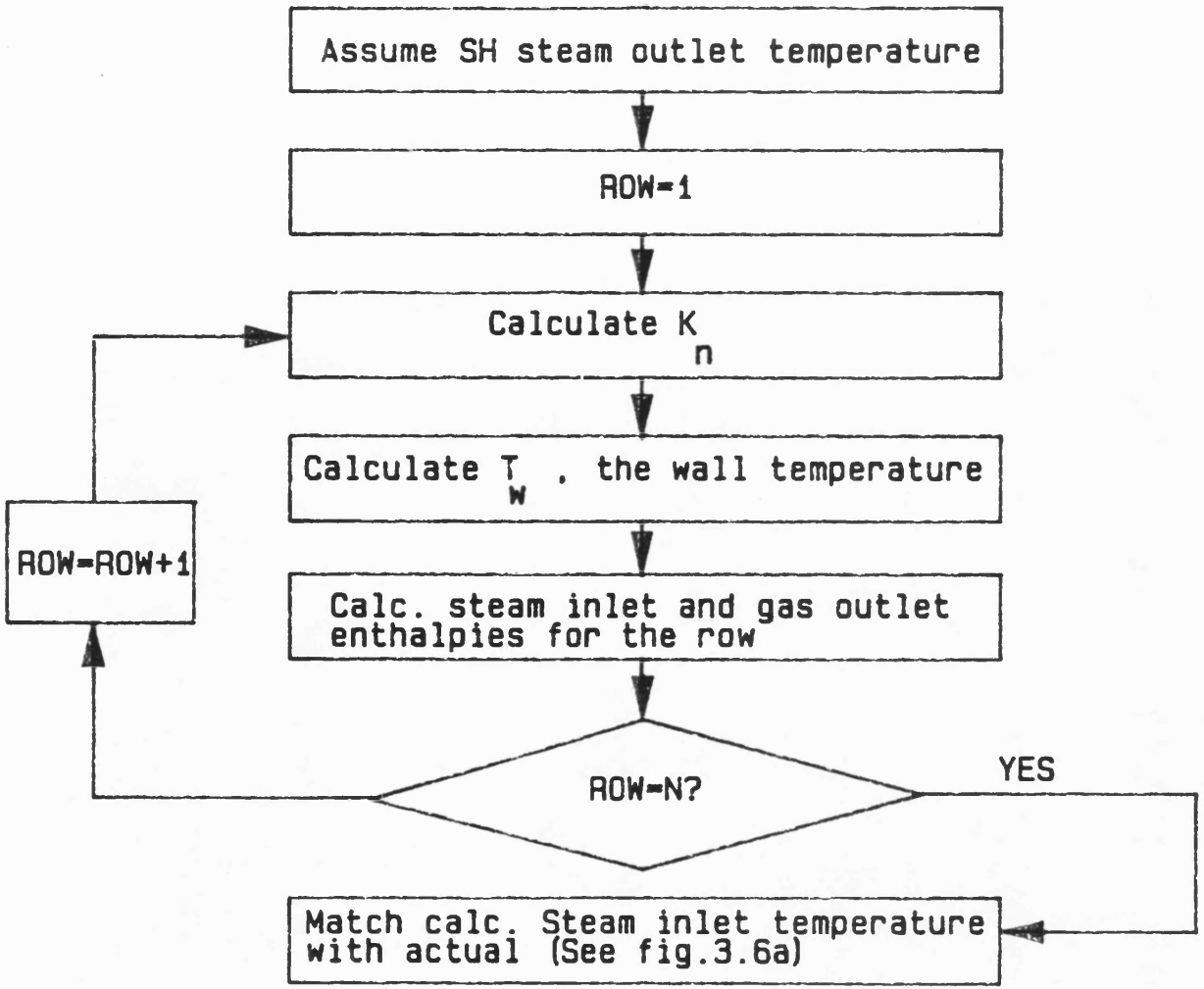


Fig 3.6 Algorithm for Superheater

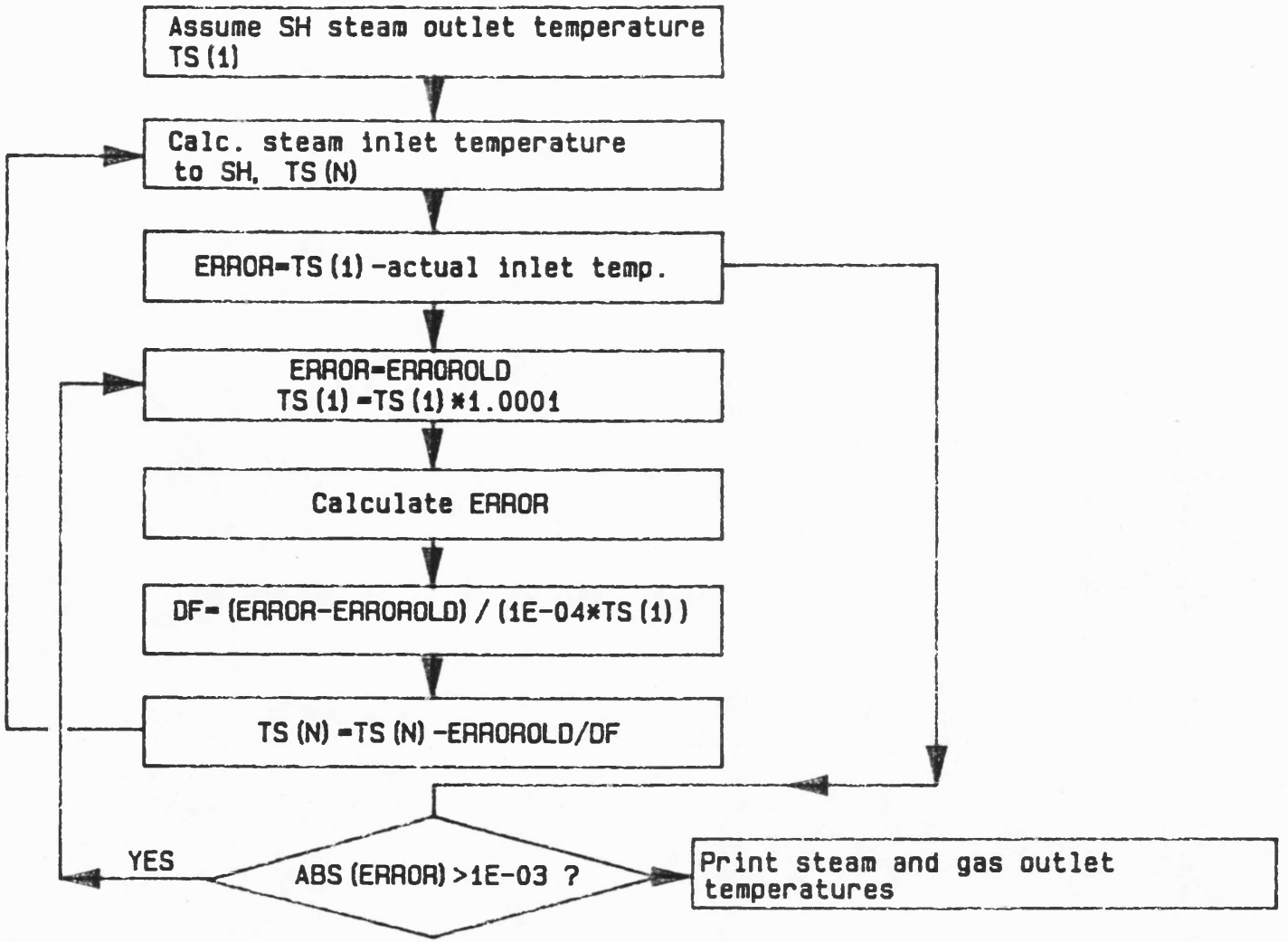


Fig 3.6a Algorithm for superheater temperatures

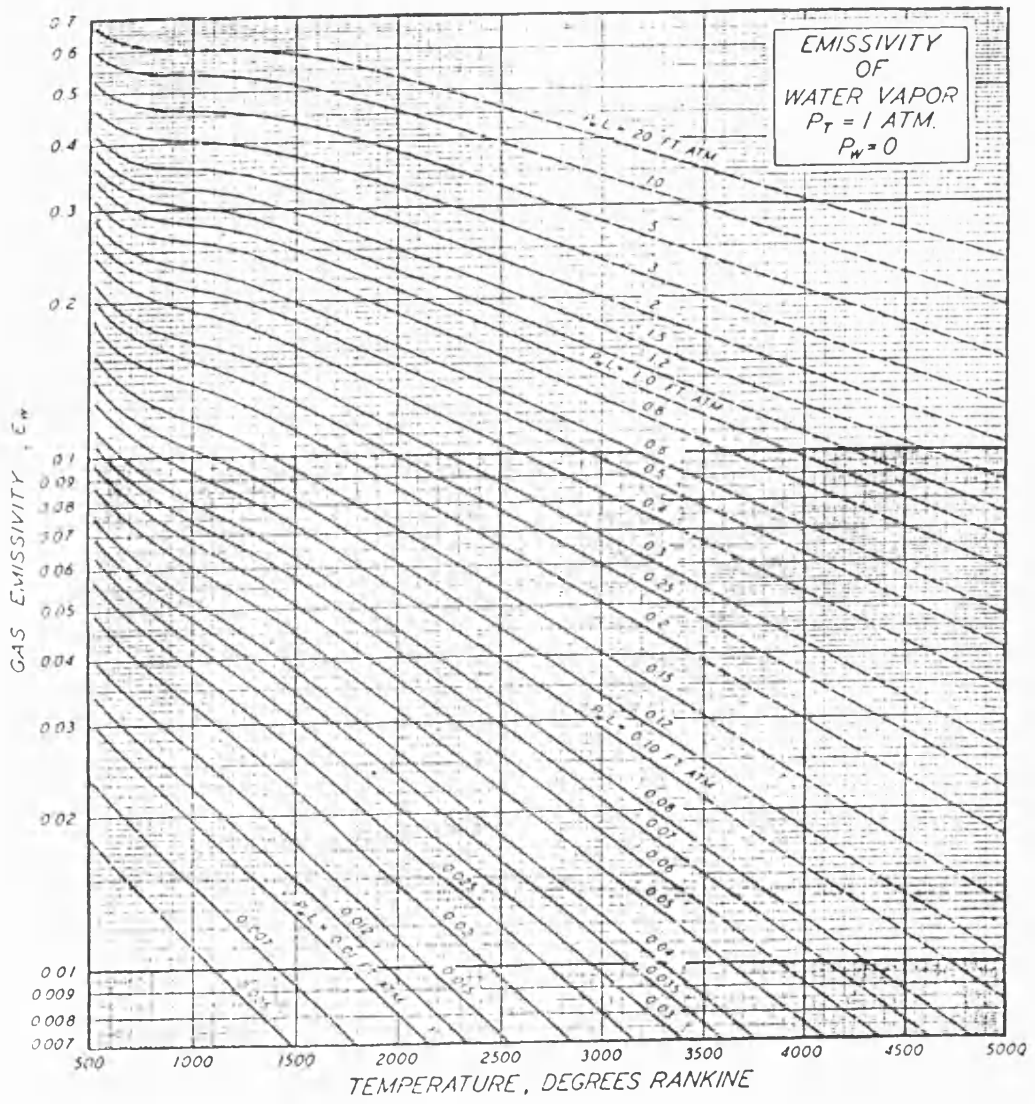


Fig 3.7 Hottel's Chart for emmissivity of water vapour

$$\sigma\varepsilon_g(T_{gs}^4 - T_w^4)A_{gs}K_n + (h_o + h_n)A(T_g - T_w) = h_i\frac{d_i}{d_o}A(T_w - T_s) \quad \text{.....(3.67)}$$

c. An exit temperature of steam from the superheater is assumed, and since T_s at the inlet to the first row is known, equation 3.67) is solved for T_w using the Newton-Raphson method. The heat transferrred to the steam can be calculated for the row. The inlet enthalpy and temperature of the steam and outlet enthalpy and the outlet temperature of the gas for the row can be evaluated.

d. The above procedure is repeated row by row down to the last row of the SH. The calculated steam temperature at the inlet of the last row of the superheater is matched against the actual temperature at which steam is being fed from the steam drum.

e. Using the Newton-Raphson iterative method, the steam inlet temperature is matched with the actual value to within specified tolerance, say 0.001 C. The corresponding enthalpy and process temperature of gas at the outlet of the superheater are also calculated.

Evaporator (EV)

As in the the radiant evaporator, saturated water from the steam drum is circulated through the evaporator tube bundle. Part of the the water flashes into steam as it flows through the evaporator leading to two phase flow conditions.

The evaporator is divided into several elements for the analyses of heat tranfer and chemical reaction. The temperature at which the oxidation of nitric

oxide commences is calculated as explained earlier in section 3.10.1.

To simulate the EV, the following algorithm as illustrated in Fig.3.8 is executed for each element.

1. The gas side heat transfer coefficient, h_o, is estimated using equation (3.42), using the inlet temperature of the element for the estimation of the transport properties. As the gas-side heat transfer resistance is the controlling one, the overall "clean" heat transfer coefficient, U_c, is estimated to be 90% of the gas side heat transfer coefficient. The overall "dirty" heat transfer coefficient in the element, neglecting the resistance of the tube wall material, is given the equation

$$U = \left(\frac{1}{0.9h_o} + f_{gs} + f_{ts} \right)^{-1} \qquad .....(3.68)$$

where f_{gs} and f_{ts} are the gas-side and tube-side fouling factors respectively.

2. The inlet temperature to the row is checked to see if it is below the temperature of commencement of nitric oxide oxidation, T_{COM}. If it is, then the conversion for that element is estimated in accordance to the procedure explained earlier in section 3.10.2. The enthalpy of gas, H_{n+1}, leaving the row is calculated from the equation :

$$H_{n+1} = H_n + HR_n - Q_n \qquad .....(3.69)$$

where H_n is the enthalpy of gas entering the row, HR_n is the heat evolved due to chemical reaction in the row and Qn is the cooling duty of the row.If the row inlet temperature is higher than T_{COM}, then the term HR_n in equation 3.69 is equal

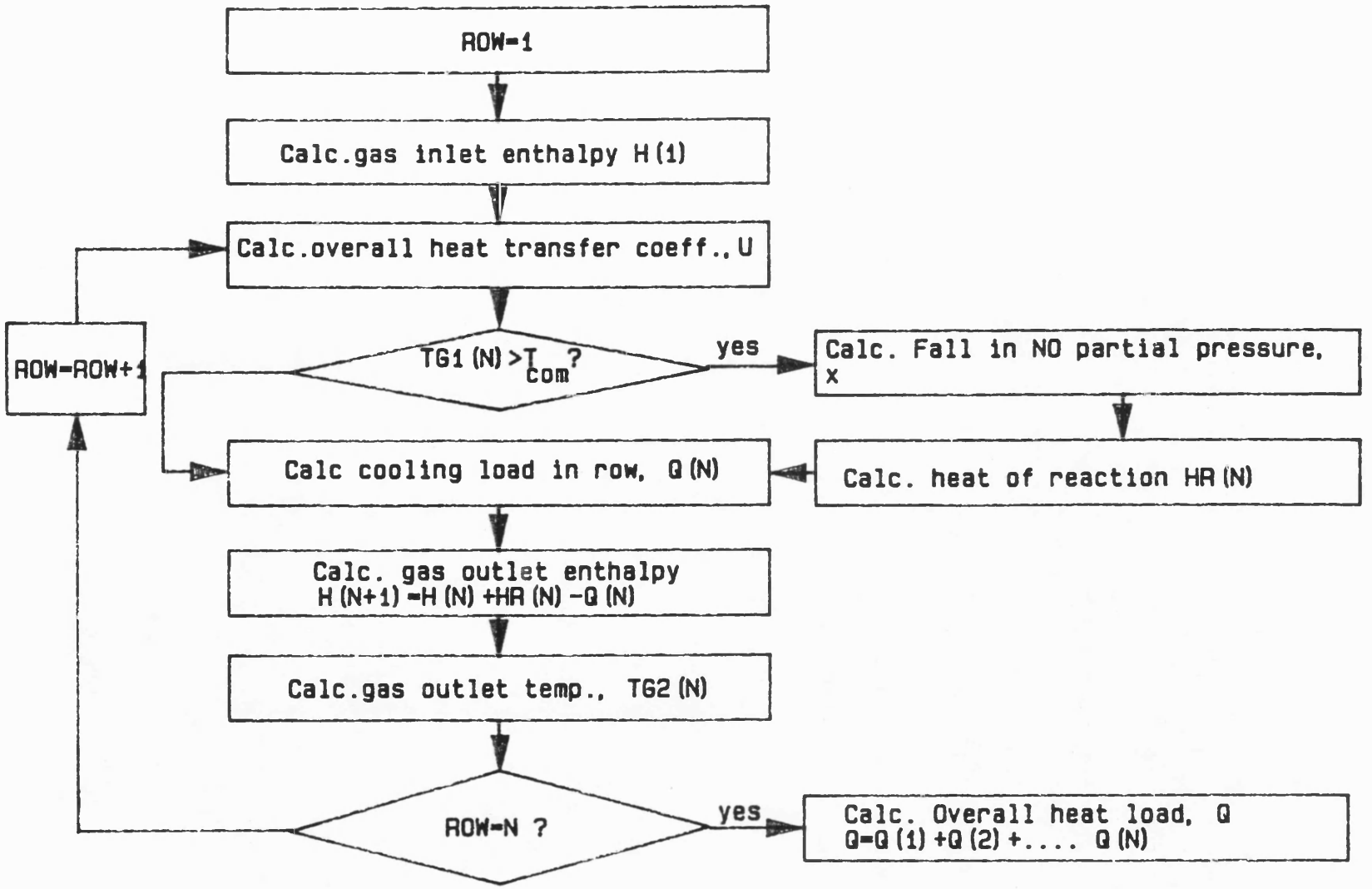


Fig 3.8 Algorithm for evaporator simulation

to zero.

3. The outlet temperature corresponding to the outlet enthalpy of the row is estimated by using the physical properties package of the SIMULATOR . This temperature becomes the inlet temperature to the next element.

4. The above procedure is repeated until the gas inlet and outlet temperatures of all the elements have been calculated.

5. The overall rate of heat transferred over the entire EV is the sum of the contributions of all the individual elements.

Economiser (EC)

The approach used for the simulation of the economiser is very similar to the one used for the EV. The only difference is that the temperature of the feedwater continuously changes as it flows through the EC, unlike the temperature of the two phase water-steam mixture in the EV which has been taken to be constant. A water temperature at the outlet of the EC has to be assumed. By carrying out the extents of heat transfer and chemical reaction in each row the gas outlet and water inlet temperatures are estimated at the inlet of the EC. The calculated water temperature at the very last element is matched against the actual temperature of the EC feedwater temperature, and a Newton-Raphson technique (similar to the one used in the SH for finding out the outlet steam temperature) is used to iterate the water temperature at the outlet of the EC and the procedure repeated until a specified error tolerance is met. As

it was not possible to develop an analytical expression for the estimation the derivative which is the rate of change of water inlet temperature to the assumed outlet temperature, numerical differentiation was used. The assumed value of the outlet water temperature was perturbed by 0.01% and the change in economiser water inlet temperature was computed. The derivative is equal to the change in economiser water inlet temperature divided by the pertubation of the outlet temperature. The tolerance limit on the convergence is 0.1%.

3.10.6 Results and Conclusions

Fig.3.9 shows the variation of gas outlet temperature with gas throughput for the RV and SH. The throughput was varied from 80 to 105% of the normal operating capacity keeping the gas inlet temperature to the WHB constant.

Fig.3.10 gives the row-wise heat-release by the process gas in the EV tube bundle. The calculations show that the variation of heat transfer coefficient is minimal. Hence the heat release rate is initially high due to the large temperature difference that exists between the process gas and the water steam mixture. The heat release rate decreases as the temperature difference reduces.

Fig.3.11 shows the variation of process gas temperature as it flows through the EV and follows the same pattern as the heat release curve in Fig.3.10.

Fig.3.12 shows the extent of oxidation of nitric oxide to nitrogen dioxide. The oxidation of NO to NO_2 is triggered off at a temperature of approximately 500°C and at the 16th row of the EV. At temperatures slightly below the triggering temperature, the conversion is low and hence the temperature profile only

Fig 3.9. Radiant Evaporator and Superheater Simulation

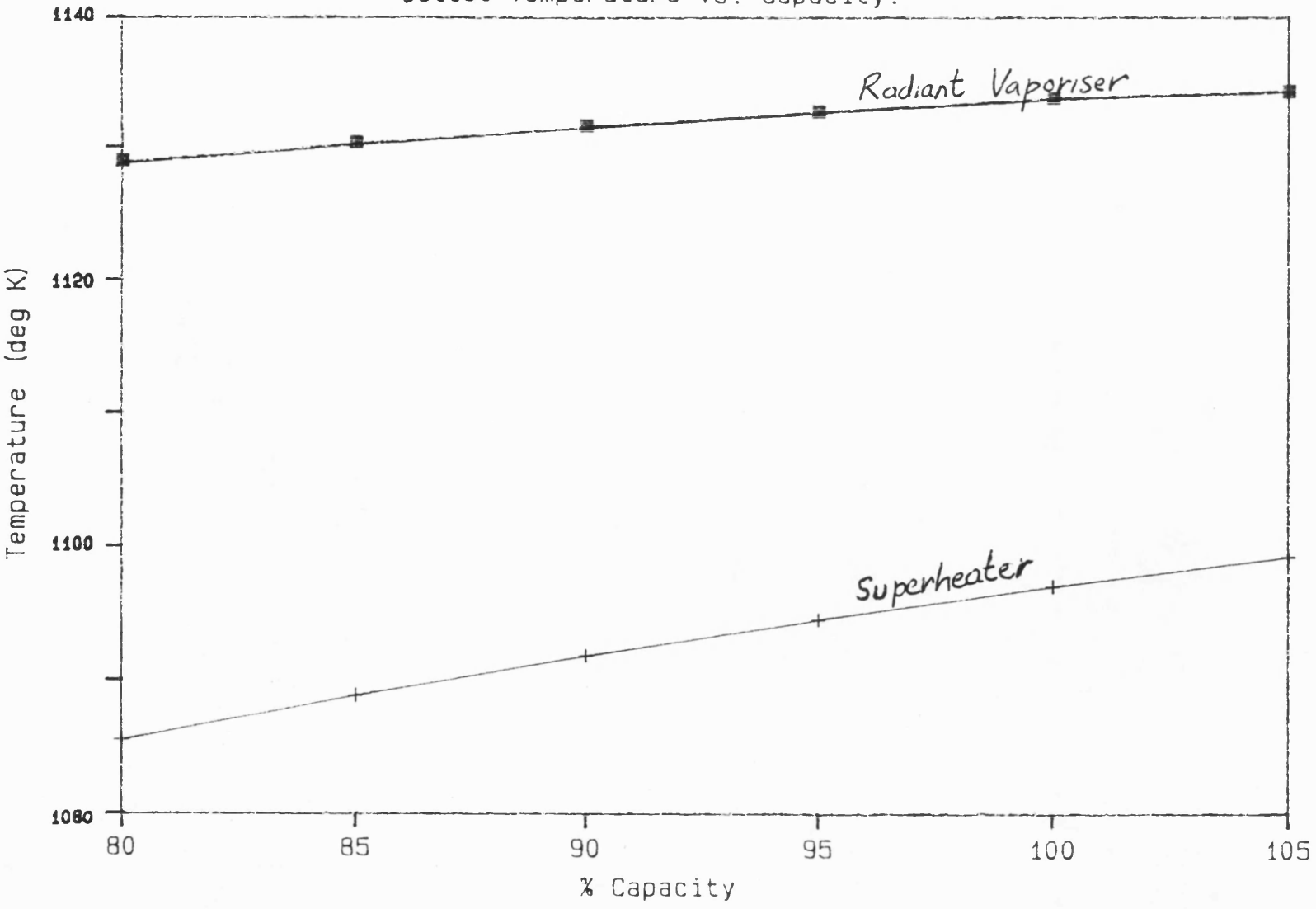


Fig 3.10 Heat release in the evaporator

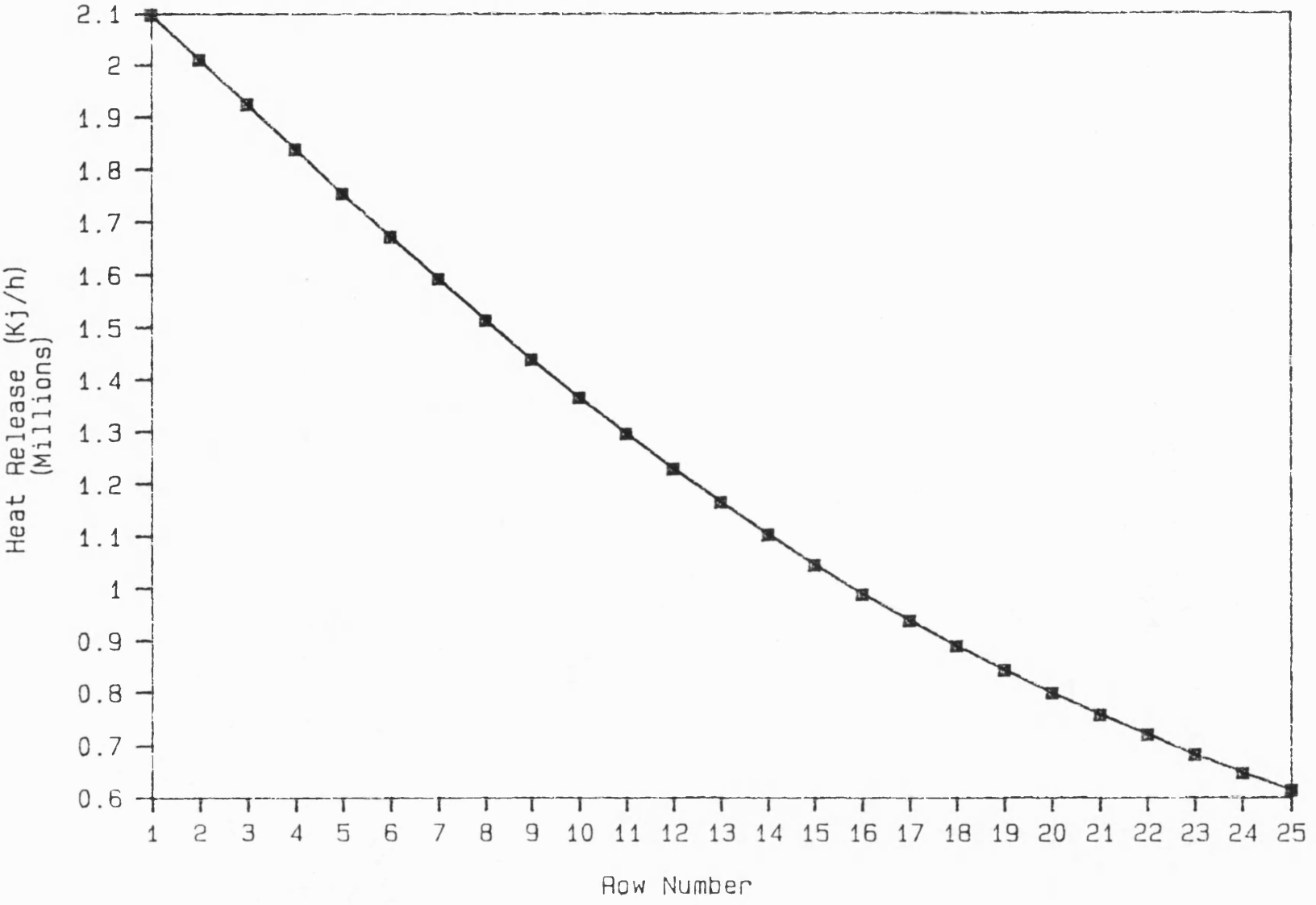


Fig 3.11 Evaporator temperature profile

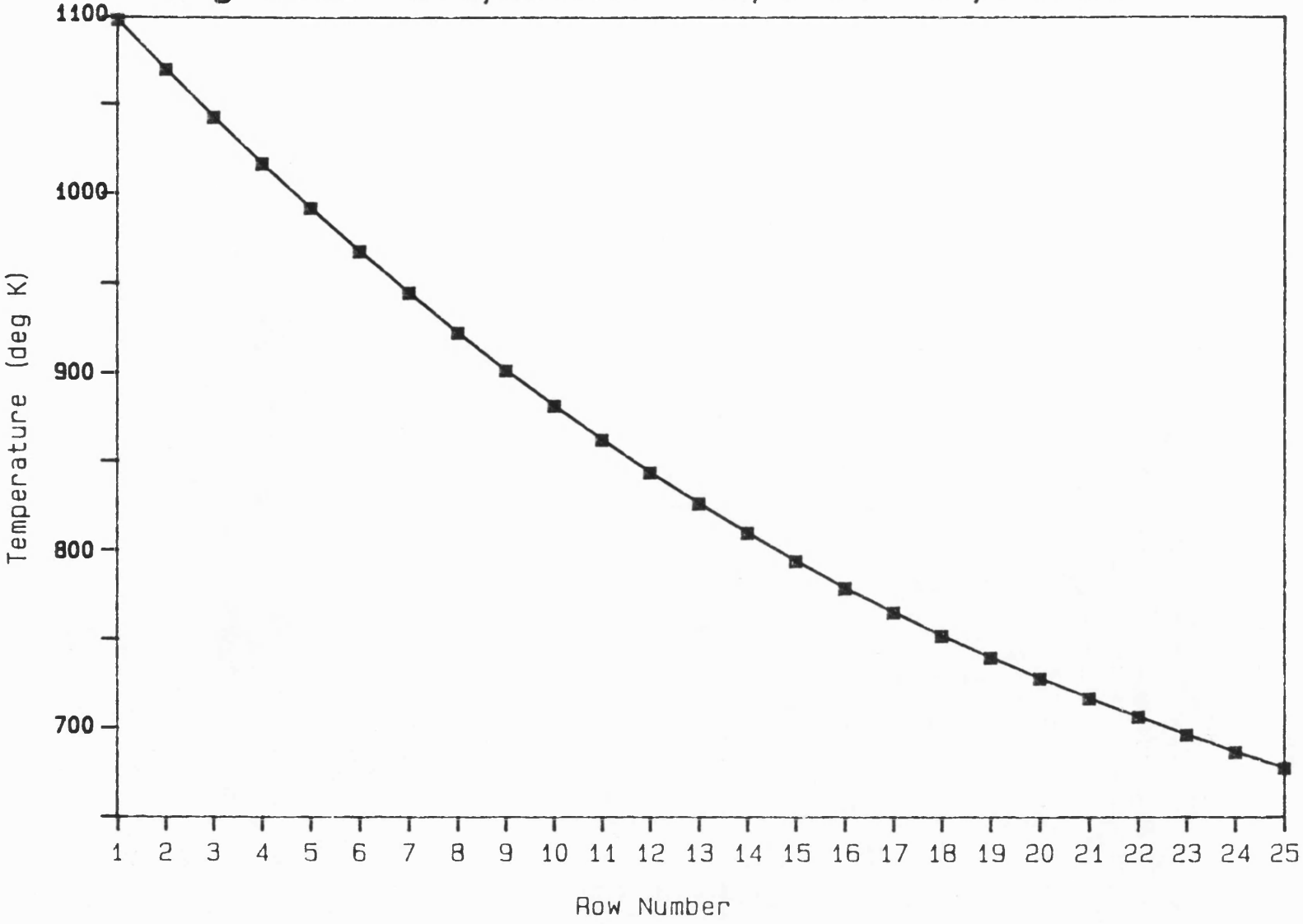
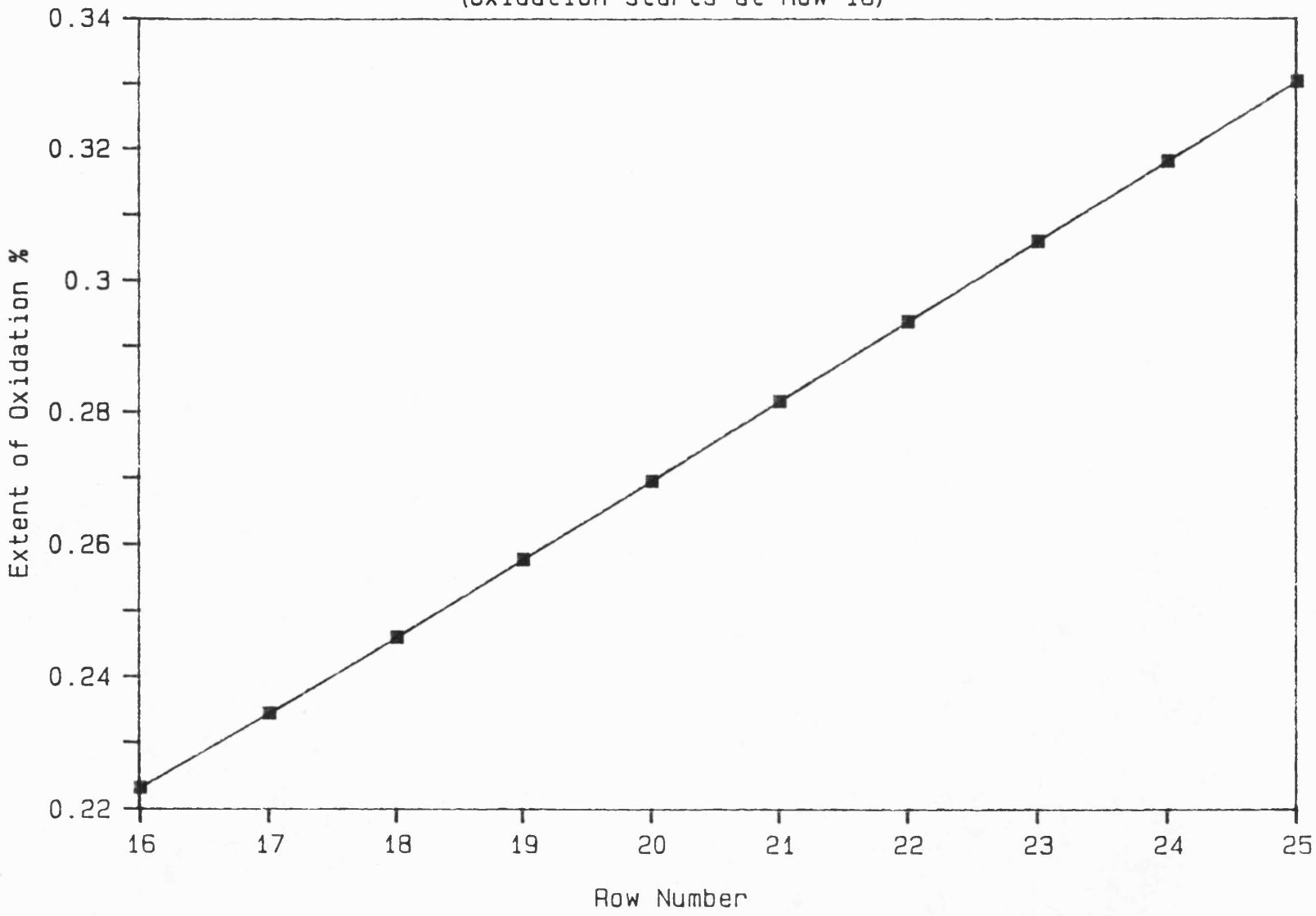


Fig 3.12 Extent of oxidation in evaporator



marginally affects the heat of oxidation. As the gas is cooled further and further the ratio of heat of reaction generated to the total cooling per row increases until it finally reaches approximately 25% at the economiser outlet.

A comparison of the results calculated with the method used by Solomon and Hodges with the same WHB inlet and outlet temperatures and NO and O_2 partial pressures shows that the oxidation of NO predicted by their method is lower by 5% than the value predicted by the present method. This is because they have used a log mean rate constant based on the inlet and outlet temperatures whereas the present work the change in rate constant with temperature is calculated in each element as the gas traverses down the WHB.

Initially while carrying the simulation of the economiser it was assumed that the water temperature at the economiser would not exceed the boiling temperature as is the case of most economisers in industry. However simulations showed that the economiser outlet temperature actually exceeds the temperature of boiling point of the water at the economiser pressure. Therefore the outlet water temperature estimation routine of the economiser module had to be modified to account for the boiling in the economiser by introducing the dryness fraction parameter. The economiser actually generates a steam-water mixture having a dryness fraction of approximately 10 to 20 % (W/W) depending on the temperature of the economiser feedwater.

The present simulation shows that the effects of the geometric aspects of the WHB such as the tube bundle configuration and dimensions, tube dimensions

and free gas areas should be accounted for in the SIMULATOR. These mechanical design variables affect the residence time gas, velocities etc. and consequently the extent of nitric oxide oxidation and heat transfer.

4.0 AUDSIM

In the operation of present day chemical and hydrocarbon processing plants, thousands of sets of measurements of various process variables are collected and recorded by data aquisition systems. These measurements can be corrupted thus causing errors of varying degrees of severity. If raw measurements which include gross errors are used for either the control or optimisation of the process the efforts would be counter-productive. Process measurements can be in error because of instrument inaccuracies or malfunction. However even when instruments are functioning normally, process variables can deviate from their normal operating band because of equipment faults. Equipment faults may be of the "traumatic" type or the "subtle" type. Examples of the former are a sticky control valve or a leaking interstage seal in a compressor, or a leaking pipe. The latter type of faults involves more gradual changes in process measurements. For example, "subtle" faults could be due to the slow deterioration of catalyst activity or caused by increase in fouling of heat exchangers.

The optimisation of an operating strategy for a process has therefore to be preceded by the identification and subsequent rectification of the various traumatic equipment faults and the instrumentation which indicate the process measurements in gross error. A number of method can be used for the diagnosis of process equipment faults. The method can be divided into two types: experience-based and logic-based. The experience based method makes use of decision tables (Berenblut, 1977) while the logic-based methods

carry out an analysis of the sequence of actuation of alarms (e.g. Welbourne, 1968 and Andow, 1975). However, the sequence of alarm actuation would be correct only if the set-points of the various alarms are accurately set. Iri et al. (Iri et al., 1980 and 1981) developed a method on based on alarm analysis where the cause of a fault could be detected even if the alarms might not have actuated in the sequence of the events occuring. The major drawback of alarm actuation analysis is that process plants may not have the number of alarms that are required to carry out a comphrensive fault diagnosis. In addition alarms may not be placed at the right locations. Andow (Andow, 1985) carried out a study on the implementation of expert systems for fault diagnosis.

An accurate picture of the operating conditions of the plant is required prior to optimisation for two reasons. Firstly it is necessary to establish if the operation of the plant is already at an optimum. Secondly, accurate information such as flowrates, pressures, temperatures etc. is needed to provide a basis for the optimisation procedures.

AUDSIM, the program developed in the present research is the software which endeavours to provide the information on the state of process operation prior to the optimisation of the process. The software downloads process variables recorded by the process database, the AUDITOR, and validates the integrity of the measurements. Input variables for running the SIMULATOR are validated using mathematical and knowledge-based validation methods. The SIMULATOR is then run and its results are used to validate the rest of the measurements. Once the validity of all the measurements is established and

providing it is confirmed that no equipment faults are detected the process measurements are passed on to the optimisation routines, In other words, AUDSIM validates and passes on measurements from a process, the equipment and control systems of which are free of traumatic faults, to process optimisation software.

4.1 Generalised Validation Method

An outline of the method is given in Fig. 4.1. Process data are continuously stored on an on-line database. For the purpose of validation, information from the process can be divided into two types: primary type and secondary type. Primary information consists of those variables (u_1, u_2, u_3,.....u_n) which are vital to the running of the SIMULATOR, while secondary information contains those variables (v_1, v_2, v_3,.....v_n) which can be verified by the results generated by the SIMULATOR.

Primary information can be further sub-divided into two types A and B:

(i) Information of Type A (uA_1, uA_2, uA_3,....uA_k) is validated using a knowledge-based expert system (KBES).

(ii) Information of Type B (uB_1, uB_2, uB_3,.....uB_l) is validated by minimising the sum of the least squares of the errors in measurement while satisfying the constraints imposed by the laws of conservation of mass and energy. In other words by using a set of mass and heat balance equations the objective function (the sum of the square of the errors) is minimised. This method will be referred to in future as mathematical validation.

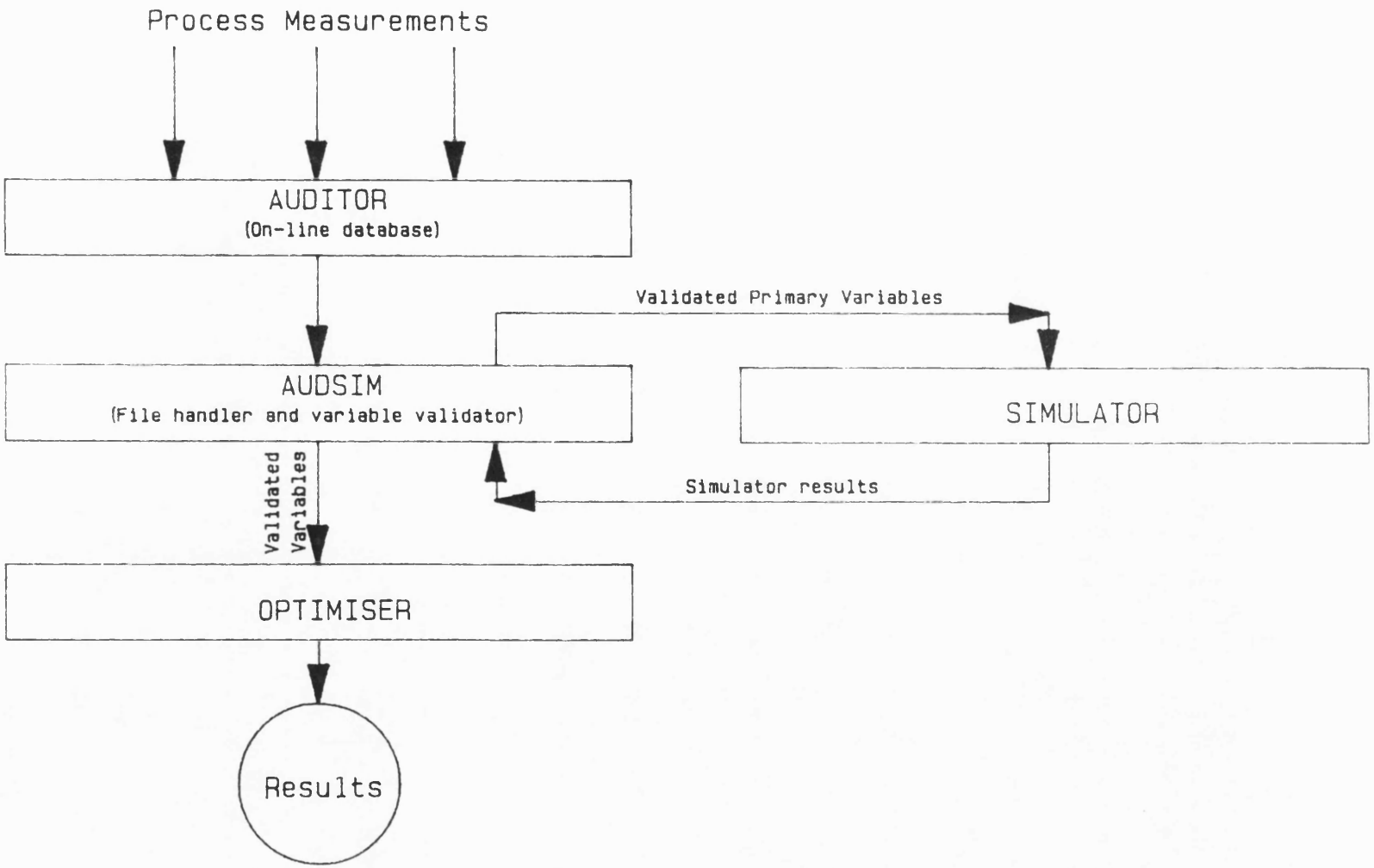


Fig. 4.1 The Methodology

Information is downloaded from the database by AUDSIM and formatted in such a manner that the primary variables (uAs and uBs) are passed on to the preliminary INFO VALIDATOR, and the secondary variables (v) are passed on directly to the final INFO VALIDATOR.

Primary information of both types A and B are validated by the preliminary INFO VALIDATOR, which incorporates the KBES and the mathematical validation program. Validated primary information is fed to the SIMULATOR.

Results of the SIMULATOR which performs the simulation of the process are passed on to the final INFO VALIDATOR, where secondary information is checked for validity. If all the information passes the validation tests, then the process optimisation modules are run and the recommendations are given to the Process Operators.

If the final INFO VALIDATOR finds that there are discrepancies in the secondary information, the INFO VALIDATOR will modify or correct them, making use of the SIMULATOR results.

4.2 Process Variable Validation

It is absolutely vital to have correct measurements of the various process variables used by the simulation and process optimisation modules. All variables recorded by the on-line database must therefore be validated.

The two types of measurement errors are systematic and random errors. Systematic errors may be inherent, that is due to the design, construction or installation of an instrument. They could also be gross errors, which are due to

the faults of the instrumentation system. Therefore systematic errors affect the accuracy of the the instrument. Random errors on the other hand produce small flucuations in the true or expected value of a measurement and could be due to changing physical property measurements caused by pressure or temperature effects. Random errors affect the reproducibility of the instrument.

Several methods have been suggested in literature for the validation of process variables, especially for the reconciliation of flow measurements. Swenker was the first to use the method of least squares, using linear mass balance equations (Swenker, 1964). This method was further developed by Hoffman and later by Vaclavek (Hoffman, 1966 and Vaclavek, 1969). Almasy extended the least squares method to heat balances (Almasy, 1969). Other methods that have been used are Kalman filters, minimisation under constraints using Lagrange multipliers (DeMeersman, 1979 and Joris and Kalitventzeff, 1987) and interval arithmatic (Himmelblau, 1985).

All the above methods can be applied to validate a set of process measurements only after checking to see that there are no gross errors in the set, or else there will be large errors in the "reconciled" measurements. Many procedures for sieving out gross errors rely on statistical analysis which assume that measurement errors are normally distributed and their variances are known. However in practice, the variance of errors may not be available and it may not be possible to assess them correctly because the errors may be random or systematic. The prediction of systematic error is difficult to evaluate because they can be caused by drifts and ageing of instruments (Lutcha, 1985). In view of

these difficulties the present research proposes to carry out validation using least squares validation with mass and heat balance constraints and using a process knowledge base for the detection of gross errors in measurements.

4.2.1 Mathematical Validation

The SIMULATOR requires accurate rates of the raw material and finished products together with the temperatures of incoming streams to yield accurate results that simulate the true behaviour of the process. Therefore it was decided to validate these important variables using the mathematical validation procedure.

The mathematical validation of a set of flow measurements is carried out by minimising the sum of the squares of the errors in measurement so that the law of conservation of mass is obeyed. In other words a process of constrained minimisation is carried out. The procedure for setting up the constraint equations based on mass balances as follows:

Make a list of the various process streams (S_1, S_2, S_3, ...S_{N_S}) entering or leaving the battery limits of the plant, and then list the various elements (atoms) contained in each stream. If the various process streams entering or leaving the battery limits have amongst them N_E elements, we can set up N_E number of independent mass balance equations any one of which can then be used as a constraint equation in the minimisation of errors in the measurement of flows of N_S streams.

Next make a list of temperatures of streams (T_1, T_2, T_3 ...T_n) to be validated

and set up suitable heat balances to act as constraints on the minimisation of errors in temperatures due to the law of conservation of energy. .

The minimisation problem is represented by the following equations:

$$\text{Minimise} \quad S = \sum_{i=1}^{n} (uB_i - \overline{uB}_i)^2 \qquad \text{.....(4.1)}$$

$$\text{Subject to} \quad uB_i = Z_j(ub_1, uB_2, \ldots .uB_i) \quad \text{for i=1 to n and j=1 to m} \qquad \text{.....(4.2)}$$

Equation (4.1) can be solved for the values of the validated or reconciled flows by substituting the variables uB_1, uB_2,....uB_i in terms of their functions Z_1, Z_2,....Z_i and setting the partial derivatives of the sum, S with respect to the variables uB_1, uB_2,...uB_i equal to zero as follows:

$$\frac{\delta S}{\delta uB_i} = (Z_j(uB_1, uB_2, \ldots .uB_i) - \overline{uB}_i\}.\left(\frac{\delta Z_j}{\delta uB_i}\right) = 0 \qquad \text{.....(4.3)}$$

It is proposed to call the flowrates of the main streams entering or leaving the process battery limits and the temperatures of streams required by the SIMULATOR (as inputs) "master measurements" (like the master gauges in a machine tool-room) which are used for validating other measurements. These master measurements are first checked for gross errors. If no gross errors are found they are reconciled or adjusted using the constrained least squares minimisation method. The validated or reconciled results thus obtained are fed to the SIMULATOR to produce a set of calculated variables which can then be used for the validation of the rest of the variables. The instruments measuring the master measurements should be calibrated on a regular, preferrably on a weekly basis, and maintained to high standards.

4.2.2 Knowledge-based validation

Knowledge-based validation of chemical process variables is defined as the use of the knowledge of expert process engineers or operators, which has been fed into a computer program called the knowledge-based expert system (KBES) to critically scrutinize process variables and check their validity.

The working sequence of the KBES is shown in Fig.4.2. First the state of plant operation is examined, i.e., whether the plant is shut down, in the process of start-up or shut-down, or under conditions of rate change or in steady state operation. This is needed because the SIMULATOR can only simulate the steady state operation of the process.

The next function of the knowledge-based validation is to inspect the master measurements to establish if they lie outside their normal operating ranges.

Lastly the knowledge-based validation checks on the quality or state measurements, i.e. primary information of Type A, (uA1, uA2, uA3,....uAn), such as the pressure and temperatures of process streams at the battery limits of the plant where mathematical validation may not be practical. For example, the effect of pressure on the enthalpy of gases is rather weak at low pressures and it will be unreliable to validate pressures from energy balances using the mathematical validation route. Therefore the knowledge-based route could be very useful in situations where pressures need validation.

Just as a process operator would scan through the log-sheet of a process plant and draw his conclusions regarding the operation of the plant, the KBES is

used to validate process measurements (other than flowrates) concerning the main process streams entering and leaving battery limits. Outliers or gross errors in master measurements are also checked by the KBES using its knowledge of the process and site conditions.

The normal operating ranges are established for temperatures, pressures etc. after interviewing experienced operators of the process plant in question and examining past process logs and other operating records. In some cases it is helpful to perform some simple process calculations. This total knowledge is put into a knowledge-base containing a set of "IF THEN" rules.

It may not be possible to define a set of general or global "IF THEN" rules because items to be validated tend to be either process specific or site specific. To illustrate this consider the following examples.

(i) Process specific variable: In a system where liquid anhydrous ammonia is stored at atmospheric pressure and then pumped to an ammonia vaporiser, the temperature measurement of the ammonia feed needs validation. The measurement can be validated by checking against the saturation temperature of ammonia at atmospheric pressure, which is -27 C. This leads to the rule:
IF the vaporiser feed temperature is less than -28 C or greater than -26 C THEN the vaporiser feed temperature is taken to be -27 C.

(ii) Site specific variable: In a tropical country where seawater is used as a coolant, its temperature at the inlet of a heat exchanger is to be validated. The seawater temperature all year round varies only by 2 C, say 26 and 28 C at the

site. The measurement can be validated by this "IF THEN" rule :

IF the seawater (coolant) temperature at the exchanger inlet is less than 26 C or greater than 28 C THEN the seawater temperature is taken to be 27 C.

4.2.3 Validation of secondary variables

Validated primary variables are transferred to the SIMULATOR as inputs. These data are used to perform the simulation of the process. The structure of the SIMULATOR and its computing algorithms have been discussed in Chapter 3. The computed results are directed back to the final INFO VALIDATOR, where the measured secondary variables are compared with the SIMULATOR results. Wherever the deviations from the SIMULATOR predictions are greater than the allowed tolerances, the secondary variables are replaced with predicted values.

4.3 Validation Specific to the Nitric Acid Process

The application of the validation procedure to the nitric acid process is discussed in the subsequent sections. The measurements being logged by the AUDITOR are listed in Table 4.1 on page 99.

4.3.1 Mathematical Validation applied to the Nitric Acid Process

An examination of Fig.3.2, shows that for the optimisation of the burner and waste heat boiler, it is sufficient that only the primary air, secondary air and ammonia flowrates are validated. However, in order to validate the air and

ammonia flows, is was necessary, as shown in Fig.4.3, to validate all the process streams entering and leaving the battery limits of the plant. The input and output streams are:

1. Primary Air.
2. Secondary air.
3. Ammonia.
4. Product acid.
5. Process water.
6. Tailgas.

In addition to carrying out the validation of flowrates of the six process streams flowrates, the temperatures of the streams entering the mixer have to be validated as the optimisation of the burner requires a validated mixed gas temperature.

Since the tailgas contains all the nitrogen introduced into the process by the primary and secondary air, the tailgas flowrate can be expressed in terms of the primary and secondary air flowrates. Strictly speaking, this is an approximation because certain amount of nitrogen is produced by the degradation of ammonia and nitric oxide in the burner. To avoid making this approximation the efficiency of conversion of ammonia to nitric oxide is used for calculating the additional nitrogen in the tailgas. The measurements of NO_x and O_2 in the tailgas are taken to be correct, if their measured values lie within specified limits, but this assumption does not significantly affect the validation of the main stream flow rates even if they are in error by ± 50 %. The same applies

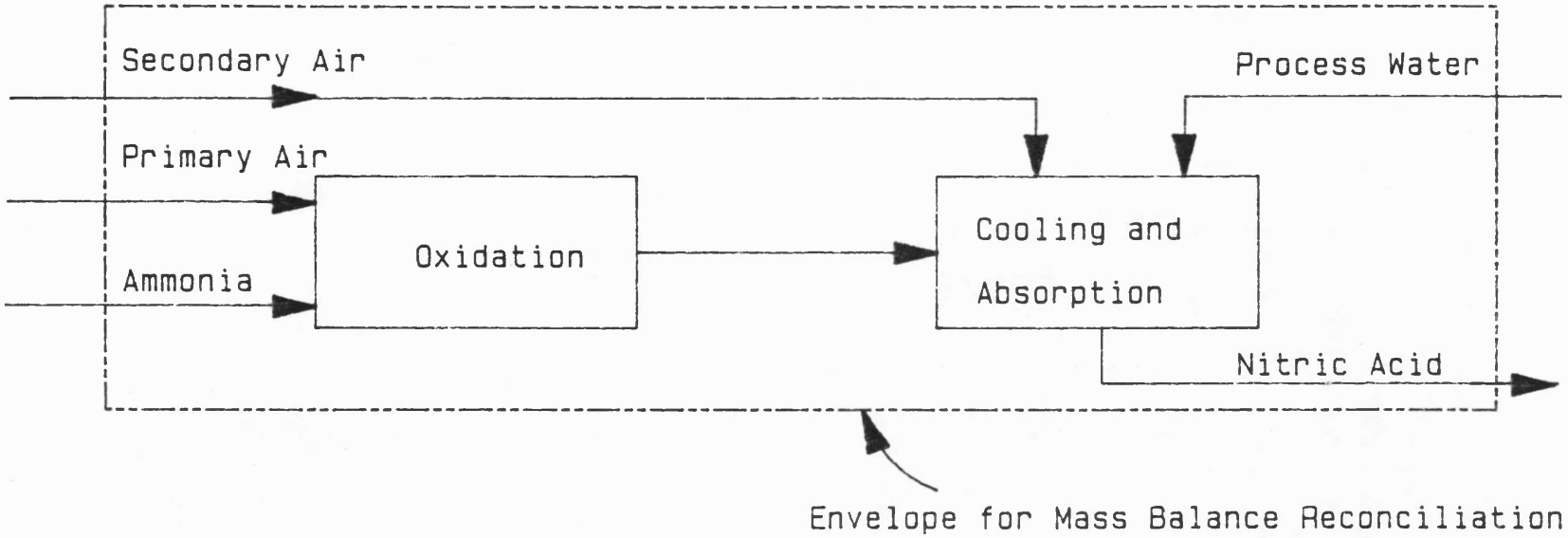


Fig. 4.3 Mass Balance Reconciliation

to the acid concentration providing the measured value lies between the specified limits of 58 to 60 % W/W. Even so the knowledge-based validation procedure checks the values of these measurements and will warn the operators if the values are outliers. The normal operating ranges of the master variables are given below:

1. Ammonia flow Range: 8500 to 10500 NM^3/H
2. Primary air flow: Range 70000-80000 NM^3/H
3. Acid flow: Range 36-40.5 Te/H
4. Process water flow: Range 7-9 M^3/H
5. Secondary air flow: Range 10000-16000 NM^3/H

Before using the master measurements, they are checked to see if they lie within or outside their normal range. When one or more of the master variables are outliers it would be safer to abort the validation procedure and find out the reason for outlying master measurements. The knowledge-base checks the ratio of ammonia flow to nitric acid flow as the ratio indicates if the plant is in a state of start-up or shut-down or the rates are being changed.

There are six streams entering or leaving the battery limits of the plant. These streams contain three elements in all. Three equations involving overall hydrogen, oxygen and nitrogen mass balances can be set up and used as constraints in the least squares mass balance reconciliation.

The following mass and heat balance equations are set up:

Hydrogen balance yields the equation:

$$NH3FLO = C_{24}\{ACIDFLO.C_8 - 0.04464C_{10}(AIRFLO + SECFLO)$$

$$- 55.56PROFLO + 0.03526\frac{C_4}{C_1}(AIRFLO + SECFLO)\}$$

.....(4.4)

where NH3FLO = Ammonia flowrate NM^3/H,

AIRFLO = Primary air flowrate NM_3/H

SECFLO = Secondary air flowrate NM_3/H

ACIDFLO= Acid flowrate Te/H

PROFLO = Process water flowrate M^3/H

C_{24} = 1/{0.6696-0.0223 (C_4/C_1)(1-Ef)}

C_{10} = (VP_1/ P(1)) - VP_1

C_1 = 1-(VP_2/ PTG+$10^{-6}C_{NOX}$+0.01 C_{O2})

C_4 = VP_2/PTG

C_8 = 55.56- 47.618 C_{HNO3} /100

Ef = Ammonia efficiency in the burner

VP_1,VP_2 = Vapour pressure of water at the ambient and tail-gas temperatures respectively.

PTG = Tail-gas pressure

C_{NOX}, C_{O2} = Nitrogen Oxides and Oxygen concentrations in the tail-gas

C_{HNO3} = Acid concentration %

Oxygen balance yields the equation:

$$AIRFLO = \left(\frac{1}{C_{26}}\right)\{C_{11}.SECFLO - C_7.ACIDFLO$$

$$-\frac{C_5}{C_1}(0.0223.(1-Ef).NH3FLO + 0.0353.SECFLO) + 27.78.PROFLO\}$$

.....(4.5)

where $C_{26} = 0.0353\ C_5/C_1 - C_{11}$

$C_5 = 10^{-6}\ C_{NOX} + 0.01\ C_{O2} - 0.5\ C_4$

$C_{11} = 0.04464\ (0.21 + 0.5\ C_{10})$

Similarly an equation for the nitrogen balance can be written.

For the validation of the mixed gas temperature, primary air temperature and the ammonia temperature, a heat balance over the gas mixer is formulated which yields the equation:

$$H(6) = H(3) + H(5)$$ .....(4.6)

where H(S) is the enthalpy of stream S, stream 3 is primary air from the tailgas heater, stream 5 is ammonia from the superheater and stream 6 is the mixed gas

Equation 4.5 can be expressed in terms of flows and temperatures of the various streams mentioned above.

$$(AIRFLO + NH3FLO).Cp(6).T(6) = AIRFLO.Cp(3).T(3) + NH3FLO.Cp(5).T(5)$$

.....(4.7)

where Cp(S) and T(S) are the specific heat and temperature of stream S

To simplify computation the pressure correction to enthalpy is neglected. This is a reasonable simplification because the pressure is only about 5 bar. The average values of the specific heat for the normal operating temperatures ranges are

estimated and substituted into equation 4.6. The normal temperature range for NH_3 is 30 to 70°C, for primary air is 130 to 150°C and for mixed gas is 125 to 150°C. The use of an average specific heat over the temperature ranges of each gas stream leads to an error of less than 0.5% in the heat balance. Substitution leads to the equation:

$$T(6) = 3.0488/(AIRFLO + NH3FLO)\{AIRFLO.0.3165.T(3) + NH3FLO.0.3952.T(5) \quad .....(4.8)$$

Equation 4.7 is used as the energy balance constraint on the least squares validation.

As all the above mass balance equations have the five master flowrate variables, any one of them can be used for substitution into equation 4.1 as a mass balance constraint. The derivatives $\delta Z_j/\delta u_i$ in equation 4.3 can either be calculated analytically or numerically, though in cases where the number of variables is small it is desirable from the point of view of saving CPU time to use analytical expressions for derivative estimation. Once the derivatives have been estimated we can set up a set of simultaneous algebraic equations in accordance with equation 4.3 and find the values of the various flows to satisfy the least squares minimisation of equation 4.1. The computer program for doing the least squares minimisation of errors in the master variables of the nitric acid process is given in Appendix 2.

4.3.1 Knowledge-based Validation applied to the Nitric Acid Process

A knowledge base containing the various rules for checking whether the

master variables lie within their normal ranges and for validating primary information of Type A, (uA1, uA2, uA3,....uAn) was constructed. The knowledge and rules are presented and discussed below for each measurement which is to be validated.

(i) As the SIMULATOR and optimisation programs have not been written to handle startup, shutdown conditions or other dynamic conditions such as rate reduction or increase, the operator is queried about the process to check if it is in the state of startup, shutdown or change of rates. In addition to the knowledge items (iv), (xi), and (xii) mentioned below, there is a stipulation that the plant is at its normal operating capacity, which in this case has been defined as 80 to 100% of the full load capacity. The KBES therefore checks the plant's operating capacity.

(ii) Compressor suction pressure. The compressor suction is open to the atmosphere and therefore the suction pressure normally varies between 14.2 to 15 psia depending on the atmospheric conditions at site. If the suction pressure, recorded by the AUDITOR falls outside the pressure range 14.2 to 15.0 psia due to an instrument error the KBES will carry forth a value of 14.7 psia by default. If desired, the operator can overide its suggestion and manually input a value if he has another source of information.

(iii) Compressor suction temperature. The compressor suction is open to the atmosphere and suction temperature is therefore equal to the atmospheric temperature. The KBES checks the compressor suction temperature against a database which holds data from the Meterological Office data for monthly

average day and night temperatures. If the KBES detects that there is something abnormal with the suction temperature then there are two options. The first is for the operator to check from some other source and then manually input the correct value. The second option is for the KBES to check against the database which holds data from the Meterological Office data for monthly average day and night temperatures.

(iv) Compressor discharge pressure. The compressor is a fixed speed axial flow compressor. Using the known or observed compression ratio of the compressor in the nitric acid plant at its normal operating range of air flowrate and the validated suction pressure from (ii), the discharge pressure can be checked. If the compression ratio is outside the normal range of 4.95 to 5.05, the KBES will assume a default value of 5, and calculate a value of the discharge pressure. The validation software in Appendix 2 has not as yet been integrated with the Met office database for the validation of the ambient air temperature. At present the operator has to refer the database and input the temperature. However at a later date the database can be integrated with AUDSIM to eliminate the need for operator dialogue.

(v) Primary air temperature to the mixer. This is a master measurement. The KBES checks if its value lies between 130 and 170 C. The operator is cautioned if the measurement is an outlier.

(vi) Ammonia temperature to the mixer. Ammonia temperature is a master measurement and values lying outside the range 30 to 70 C result in a warning to the operator.

(vii) Ammonia pressure to the mixer. The pressure of ammonia to the mixer is usually 4 to 5 psig lower than the validated compressor discharge pressure. If the value lies outside this range the operator is warned and queried by the KBES about the possibility of the malfunctioning of ammonia filters. If the operator confirms that the filters are functioning normally, the default value for the ammonia pressure is taken as the compressor pressure minus 4 psig.

(viii) Mixed gas temperature. This is a master measurement and lies in the range of 125 to 150 C. If a value lies outside this range the operator is immediately warned.

(ix) Economiser feed-water temperature. This measurement normally lies between 115 to 145°C. The water temperature in the deaerator is validated against the saturation temperature of deaerating steam at the deaeartor drum pressure. Equilibrium between vapour and liquid in the drum is assumed. To allow for heat loss the economiser feed temperature is taken to be 2 C less than the deaerator water temperature. As the deaeration steam pressure is not recorded by the AUDITOR, the KBES asks the operator to manually check the deaeration drum pressure and input the value.

(x) Export steam pressure. The steam pressure should be in the range of 220 to 230 psig and is tightly controlled as the steam is being fed into the steam grid on site. If the measurement falls outside this range, the KBES assumes a value of 225 psig by default but recommends that the operator actually checks the pressure against a locally mounted gauge.

(xi) NO_x Level at the abator inlet. The NO_x level at the abator inlet under

the normal process operating load of 8800 to 10000 NM^3/h of ammonia should be in the range of 3500 to 5000 ppm. If the value for the normal operating load lies outside this range, the operator is informed and a default value of 4000 ppm is assumed. Had the scope of the SIMULATOR included the entire process, this variable would have actually been a secondary variable.

(xii) Oxygen in the tailgas. The oxygen content in the tailgas at normal process operating loads is between 0.6 to 0.8 % v/v. A default value of 0.7 % is taken if the measured oxygen content at normal operating loads falls outside the specified range. As in the case of the NO_x measurement at the abator inlet, the oxygen measurement in the tailgas would have been a secondary variable had the SIMULATOR covered the entire process.

(xiii). Process water. This is a master measurement, and should lie in the range of 7.0 to 9.0 M^3/h. If the KBES detects that this measurement lies outside the above range the operator is warned.

Rules have been developed on the basis of the knowledge discussed above. They are:

A. Rules for checking startup, shutdown or change of rates:

1. IF either the ammonia or air rates were changed in the past 30 minutes THEN abort the validation and warn the operator.
2. IF the air rate is less than 70000 NM^3/h or greater than 78000 NM^3/h THEN warn the operator.
3. IF the ammonia rate is less than 8500 NM^3/h or greater than 10500 NM^3/h

THEN warn the operator.

B. Rules for checking the master measurements:

4. IF the primary air temperature to the mixer is less than 130 C or greater than 170 C THEN warn the operator.

5. IF the ammonia temperature to the mixer is less than 30 C or greater than 75 C THEN warn the operator.

6. IF the mixed gas temperature is less than 125 or greater 150 C THEN warn the operator.

7. IF process water flow is less than 7 M^3/h or greater than 9 M^3/h THEN warn the operator.

C. Rules for checking the rest of the measurements:

8. IF the compressor suction pressure is less than 14.2 psig or greater than 15 psig THEN compressor suction pressure by default is 14.7 psig.

9. IF the compressor suction temperature is less than 0.7 times or greater than 1.3 times the value given by the Metrological Office database THEN ask the operator for the ambient temperature.

10. IF the operator can provide a correct value for the ambient temperature from another source THEN the compressor suction pressure is set equal to the ambient temperature OR ELSE the compressor suction temperature is equal to the ambient temperature according to the Meterological Office database.

11. IF the compressor discharge pressure at the normal operating range of the

process is less than or greater than 4.95 to 5.05 times the validated suction pressure THEN the discharge pressure is equal to five times the validated suction pressure.

12. IF the ammonia pressure to the mixer is less the validated compressor discharge pressure minus 5 psig or greater than the validated discharge pressure THEN the ammonia pressure is equal to the validated discharge pressure minus 3 psig.

13. IF the economiser feedwater temperature is less than 115 C or greater than 140 C THEN the economiser feedwater temperature is set equal to the saturation temperature based on the deaerating steam pressure.

14. If the NO_x measurement at the normal operating range of the process is less than 3500 ppm or greater than 5000 ppm THEN the default value for the NO_x is taken as 4000 ppm.

16. If the oxygen measurement at the normal operating range of the process is less than 0.6 % or greater than 0.8 % V/V THEN the default value for the oxygen measurement is taken as 0.7 % V/V.

4.4 "Low-level" fault diagnosis

The measurements that are validated by the KBES are checked by a "low-level" fault diagnosis system which has been integrated with the KBES. "Low-level" fault diagnosis means the detection of faults with process systems or units, eg. the absorption system in the nitric acid process or the primary reformer in an ammonia process. This is in contrast to detailed fault diagnosis of

unit or system components like pumps, piping valves etc. as considered by Andow (Andow, 1985).

If faults in the system are detected, these defects are rectified prior to optimising the operation of the plant. If on the other hand, measurement errors are detected due to faults in instrumentation, the measurements are replaced by values from the expert knowledge of the operators. The working of the proposed fault diagnosis system is applied to the absorption system of the nitric acid process to distinguish between traumatic faults in the absorption system and faults of instrumentation.

If the NO_x level in the tailgas from the absorption system is higher than the normal range then there are two possibilities. The first possibility is that there could be a failure in the operation of the absorption system. The other possibility is that the instrument which measures the NO_x level in the tailgas is malfunctioning. The absorption system as described earlier consists of packed beds where acid is recirculated in each bed after it is cooled in an external heat exchanger. The two main reasons why the absorption system could malfunction are due to poor acid circulation or insufficient acid cooling. Hence when the NO_x in the tailgas is high the operator is queried if all the acid circulation pumps and the acid cooling exchangers are functioning normally. If the operator confirms that there are traumatic faults in either or both of the above then the optimisation of plant is aborted until the faults with the working of the absorption system are rectified. If however, the acid circulation and cooling are in operation without any traumatic fault it is concluded that the instrument measurement is in error.

The erroneous measurement is then replaced with a value using the expert knowledge of the operator.

Hence this low-level fault diagnosis is used to establish whether an outlying measurement is due to equipment failure or instrument failure. It does not however go into the details of why there is a certain system or equipment failure. For example, the low-level fault diagnosis will not be able to tell whether the electric motor of one of the circulation pumps has burnt-out or tripped. This task is left to the operators to check the panel boards or the plant itself prior to answering the queries of the KBES.

4.5 Choice of language for knowledge based validation.

The languages that are popularly used for the construction of expert system shells are LISP and PROLOG. These languages are specially suited to symbolic handling, i.e. for the processing of character strings or lists, just as FORTRAN, BASIC or Pascal are procedural languages for numerical computing. The requirement in knowledge-based validation is to carry out both symbolic handling and numerical processing. Symbolic handling is used for the dialogue between the operator and the knowledge-base and numerical processing is needed when knowledge is represented in the models. Since BASIC was used for the SIMULATOR source code, it was decided to use the same language for developing the knowledge base as well, even though it may not be very appropriate for symbolic handling.

4.6 File Handling system

Fig. 4.4 shows the structure of the file handling system. It was required by site conditions that AUDSIM be implemented on an IBM personal computer, model PC/XT. Consequently the AUDITOR log resident on a DEC 11/23 mini-computer containing relevant process information had to be downloaded to the IBM PC/XT environment.

The process of downloading AUDITOR files was achieved by using Smar Term 100, a piece of software (Persoft Inc., 2740 Ski Lane, Madison, WI 53713, U.S.A.) which enables the IBM PC/XT to emulate the DEC VT 100 terminal. A communications cable links between the DEC computer to the IBM PC/XT. The cable from the DEC computer was connected to the RS-232 port of the IBM PC/XT.

Smar Term 100 makes the IBM PC/XT capable of emulating the "VT-100" terminal of a DEC 11/23 computer and transfer data being logged on the mainframe to the IBM PC/XT environment using a facility called the "Capture" mode. The "captured" data is ported for storage into a datafile on either the floppy disk drive or the hard disk. A datafile called "AUDINF.PRN" is created under the IBM PC DOS (disk operating system) format which makes futher work on the data possible using commonly available IBM PC software. In other words, the data regarding the snapshot of the process measurements taken by the data capture facility are stored for further processing such as validation, simulation and optimisation using programs and software, e.g. AUDSIM etc. on the IBM PC/XT.

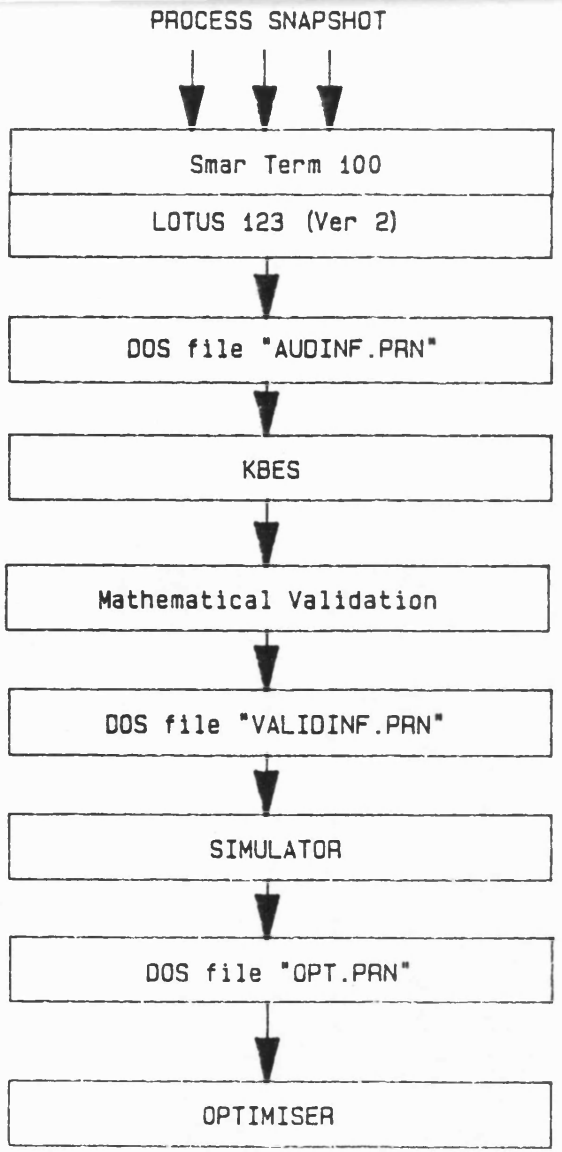


Fig. 4.4 File Management System

The datafile "AUDINF.PRN" containing the data to be fed into AUDSIM for validation is prepared by taking an average of several snapshots of the process over a 30 minute period.

Next, the datafile "AUDINF.PRN" is imported into a spreadsheet software called Lotus 123, Release 2 (Lotus Development Corporation, 55 Cambridge Parkway, Cambridge, MA 02142, U.S.A.). Using macros commands for automatic execution, a Lotus 123 file called "AUTO123.WK1", AUDITOR information is formatted into primary and secondary variables ready to be relayed to the preliminary and final INFO VALIDATORs.

Primary variables are put together after the completion of validation into a file called "VALIDINF.PRN" and sent on to the SIMULATOR. The SIMULATOR validates the secondary variables and sends both primary and secondary variables to the OPTIMISER in a file called "OPT.PRN".

#	Measured Variable	Type
1	Compressor suction pressure	Primary, Type A
2	Compressor suction temperature	Primary, type A
3	Compressor discharge pressure	Primary, type A
4	Compressor discharge temperature	Secondary
5	Air temperature to the mixer	Primary, type A (master)
6	Ammonia temperature to the mixer	Primary, type A (master)
7	Ammonia pressure to the mixer	Primary, type A
8	Mixed gas temperature	Primary, type A (master)
9	Primary air rate	Primary, type B (master)
10	Secondary air rate	Primary, type A (master)
11	Ammonia rate	Primary, type B (master)
12	Process Water rate	Primary, type B (master)
13	Gauze outlet temperature	Secondary
14	Economiser water temperature	Primary, type A
15	Gas outlet temperature at boiler exit	Secondary
16	Export steam temperature	Secondary
17	Export steam pressure	Primary, type A
18	NO_x at abator outlet	Primary, type A
19	Oxygen in the tailgas	Primary, type A
20	Nitric acid rate	Primary, type A (master)

Table 4.1 List of variables.

5.0 OPTIMISER

The OPTIMISER is the computer program for the optimisation of the operating strategy of the process. The operating strategy can vary according to the constraints or priorities set by costing, product mix, quality, throughput and safety considerations. A firm operating two identical process plants at two different sites may adopt totally different operating strategies to suit local site conditions. The important requirement of any optimisation effort is to clearly define the optimisation goals and if possible express the goal mathematically in the form of an objective function. The factors that affect the choice of the method are:

(i) Single or multi-variable.

(ii) The existence of constraints

(iii) Linear or non-linear optimisation.

Depending on the complexity of the optimisation problem one can choose the most appropriate method for the task. Some broad categories of methods are described in Chapter 2.

In the subsequent sections the optimisation of the nitric acid process will be described.

5.1 The optimisation objectives for the nitric acid process.

The nitric acid plant was carefully studied and decisions were made as to which units of the process should be optimised. The criteria used for selecting which sections of the plant to be optimised were:

(i) The identification of the need to optimise, i.e. carrying out a feasibility study by estimating the potential savings that would accrue if process optimisation was implemented without violating plant safety requirements or environmental standards.

(ii) The quality and extent of process information being collected by the data aquisition system, AUDITOR, which may or may not make certain optimisation goals technically feasibile.

(iii) The availability of process control equipment to make the optimisation possible.

The need for optimisation of operating strategy was established in three units of the nitric acid process. These units are:

(i) The first unit is the burner where ammonia is catalytically oxidised to nitric oxide over a number of platinum gauzes. The main reaction as discussed in Chapter 3 is the one which produces nitric oxide. However there are three other "loss-making" side reactions that could take place. These "loss-making" reactions are the direct degradation of ammonia to nitrogen, the formation of nitrous oxide and the reaction between ammonia and nitric oxide to form nitrogen. The objective for optimisation of the burner is to to cut down the ammonia loss through the side reactions, i.e. to achieve a high ammonia efficiency.

(ii) The second unit where optimisation may possibly be implemented is the energy recovery from the process gas in the waste heat boiler. The objective here is to cool the process gas to the maximum possible extent thereby extracting the maximum energy. At the same time it is desirable to maintain a safe "approach"

temperature to the dew-point of nitric acid in the process gas. The dew-point varies with the ammonia to air ratios used in the burner and the extent of oxidation of nitric oxide as the gas is being cooled in the waste heat boiler.

(iii) Lastly, it is desirable to optimise the operation of the absorption system which consists of four packed columns where the oxidation and absorption of nitrogen oxides in the process gas takes place. The production of nitric acid in the packed columns is a process of simultaneous absorption and chemical reaction (Andrews and Hanson, 1961). The optimisation goal is to maximise the absorption of the oxides of nitrogen to give the maximum yield of nitric acid per unit quantity of ammonia fed to the burner. This can be made possible by adjusting the acid circulation rates in each of the packed bed section according to the operating capacity of the process. In an absorption system using packed beds it is not possible to use a stoichiometeric amount of process water for absorption as is possible in the case of a sieve plate column. This is because packed beds require a certain minimum liquid flow called the minimum wetting rate to wet all of the tower packing. Therefore acid is recirculated in each of the packed beds after being cooled in external acid coolers. On the other hand, if the recirculation rate is excessively high, gaseous nitrous acid which is a component of the nitrogen oxides process gas actually by-pass the packing by dissolving in the acid at the bottom of the bed. A part of the dissolved nitrous acid then flashes back from the recirculated acid into the process gas at the top of the column, thus bringing down the efficiency of absorption. Therefore there is need to optimise the circulation rates for different operating capacities of the plant to maximise the

absorption of gas.

The extent and quality of process information being collected by the data aquisition system, AUDITOR, was critically examined with reference to the three optimisation goals in mind. It was found that the collection of information and quality of instrumentation were adequate for the optimisation of the burner and the waste heat boiler but insufficient for optimising the absorption system. It was therefore decided to limit the scope of the OPTIMISER to the burner and waste heat boiler.

5.2 The optimisation of the Burner

The model development for the burner has been discussed in Chapter 3. The ammonia efficiency, i.e. the fraction of ammonia that is converted to nitric oxide has been correlated with the ammonia flow rate, the ammonia concentration and the burner feed gas temperature. The correlation was developed after carrying out parameteric studies of the performance of the burner using a detailed burner model which took into consideration process design and detailed engineering as implemented on the burner. Some of these design and engineering aspects include the number of platinum gauzes, diameter of the burner, radiation effects, gauze geometry etc. In the parameteric model of the burner the ammonia efficiency, Ef, of the burner is correlated with the ammonia flowrate, F, ammonia concentration,C, and feed gas temperature, T_p by the following equation.

$$Ef = A1 + A2F + A3T_F + A4C$$
$$+ A5F^2 + A6T_F^2 + A7C^2$$
$$+ A8FT_F + A9T_FC + A10CF \quad \text{....(5.1)}$$

where A1, A2,...A10 are empirical constants.

The nitric acid production is fixed by the operators depending on production needs. For a certain nitric acid production rate the ammonia rate is fixed and cannot be used as a variable for optimisation.

The ammonia efficiency increases with preheat temperature of the feed gas. As the preheat temperature is increased the gauze temperature increases. However the maximum gauze temperature is limited to between 900 to 915°C as the platinum loss increases dramatically above these temperatures. Consequently the preheat temperature is limited by the maximum permissible gauze temperature. In the process under consideration, the energy recovery system has been configured such that hot primary air from the compressor is used to reheat tailgas from the absorption system prior to NOx abatement. The above flowsheet considerations does not make it possible to alter the preheat of the burner feed. As a result the only variable that we are left with to optimise is the concentration of ammonia being fed to the burner.

The ammonia efficiency is given by equation 5.1 as a function of the ammonia concentration. As the objective function is a simple single variable function, optimisation using the calculus of maxima and minima is preferred to other methods such as Golden Section or Fibonacci methods. The optimum ammonia concentration at which the maximum ammonia efficiency occurs

calculated by differentiating equation 5.1 with respect to the ammonia concentration and equating the derivative to zero.

$$\frac{dEf}{dC} = A4 + 2A7C + A9T_F + A10F = 0 \qquad .....(5.2)$$

Equation 5.2 can be manipulated to give an equation for the optimum ammonia concentration, C_{opt} when the ammonia rate and feed gas temperature are known.

$$C_{OPT} = \frac{-1}{2.A7}(A4 + A9T_F + A10F) \qquad .....(5.3)$$

5.3 Optimisation of the Waste Heat Boiler.

The model developed for the simulation of the WHB has been described in detail in Chapter 3. The energy recovery in the WHB depends on the exit process gas temperature. However, if the gas temperature is reduced sufficiently the gas will reach its dew point and nitric acid condensation will commence. As the entire boiler is built of carbon steel it is susceptible to the corrosive attack of nitric acid condensate if the dew point is reached. It is therefore desirable for safety reasons to keep the tube wall temperature at a value which is say 15 or 20 C above its dew-point. The possibility of the gas reaching the dew-point is highest at the bottom of the economiser tube bundle where the feedwater and the tube wall temperature is low.

In the development of an algorithm developed for the calculation of the dew-point of the process gas the following empirical (proprietory) equations are

considered:

(i) The gas phase equilibrium constant, K_4, for the formation of dinitrogen tetraoxide which is formed as a dimer of nitrogen dioxide by the reaction, $2NO_2=N_2O_4$, is

$$K_4 = -21.244 + 6891.61/T \quad \text{.....(5.4)}$$

(ii) In the presence of acid the gas phase equilibrium between nitrogen dioxide and nitric oxide is given by the equation:

$$\text{Log}_{10}\frac{P_{NO}}{P_{NO2}^3} = G1.T^{E1} + G2.T^{E2}C_{HNO3} \quad \text{.....(5.5)}$$

(iii) The water vapour in equilibrium with acid is given by the equation:

$$P_{H2O}^E = G3.10^{E3-E4/T}(1 - G5.W - G6.W^2 + +G7.W^3) \quad \text{.....(5.6)}$$

where G1, G2,...G7 and E1, E2,...E4 are empirical constants

5.3.1 Calculation of dew point of process gas.

The procedure for calculating the tube wall temperature at which the gas reaches its dew-point is as follows:

(i) An initial guess value for the tube wall temperature at which the dew-point occurs is assumed.

(ii) The conversion of nitrogen dioxide to dinitrogen tetraoxide at the assumed wall temperature is calculated. For this purpose the initial partial pressure of nitrogen dioxide and temperature are taken to be those at bulk gas conditions. The amount of nitrogen dioxide converted should satisfy the following equation:

$$P_{NO2_{bulk}} = P_{NO2_{wall}} + 2P_{N2O4_{wall}} \quad \text{.....(5.7)}$$

(iii) The concentration of acid at the assumed tube wall temperature that can equilibriate with the gas at the assumed tube wall temperature is estimated by equation 5.5.

(iv) The partial pressure of water vapour in the gas that is in equilibrium with the acid at the tube wall temperature is calculated using equation 5.6. If the actual water vapour content of the bulk gas is higher than the calculated amount condensation will take place. If on the other hand the actual water in the process gas is less than the amount calculated then the tube wall will stay dry.

(v) The condition for the dew-point to be reached is given by the equation:

$$P^{E}_{H2O} - P_{H2O} = 0 \qquad \text{.....(5.8)}$$

where p_{H2O} is the partial pressure of water vapour in the gas.

The wall temperature is iterated using a Newton-Raphson procedure until equation 5.8 is satified to within a tolerance of 0.1°C.

5.3.2 The optimimum feedwater temperature

To find the optimum feedwater temperature to the economiser for a given set of process conditions, the first step to be taken is to run the SIMULATOR and find out the process gas temperature and its composition at the point where the gas is leaving the last tube row in the economiser. Based on this temperature and composition the dew-point is estimated using the procedure explained in 5.3.1. A dew-point approach temperature (temperature difference between the minimum allowable tube wall temperature and the dew-point) is fixed, say at 15 to 20°C. Knowing the dewpoint the minimum allowed wall temperature, T_w is estimated. Then the minimum permissible economiser inlet water temperature,

T_{OPT} is calculated from the following heat flux equation.

$$T_{OPT} = T_w - \frac{H_O}{H_{io}}(T_g - T_w) \qquad \text{.....(5.9)}$$

The optimum economiser feed water temperature estimated from equation 5.8 is on the conservative side because fouling resistances have been neglected. For increased accuracy the fouling factors can be incorporated into equation 5.8.

6.0 RESULTS AND DISCUSSION

The working of the software to optimise the operating strategy of the process is presented in the subsequent sections.

6.1 Run Number 1

In run number 1 (Pg 113), the software is used to optimise the operating strategy of nitric acid plant number 2. In response to the question of whether the plant is being started up or shut down the operator replies in the affirmative. The KBES aborts the validation process as the software is designed only to handle steady state operation. The user is advised to optimise the operating strategy after 30 mins of steady state operation.

6.2 Run Number 2

Run number 2 (Pg 114-117) demonstrates the use of the optimisation software for the nitric acid plant number 3. The user confirms that the plant is neither being started up or shutdown and that it has been in steady state operation for more than 30 mins. The KBES checks the master variables and finds that there are no outliers. As the Met Office database is yet to be interfaced with the KBES manual intervention is required to validate the ambient temperature. The user confirms that the temperature is correct. Next the KBES checks the rest of the primary variables of type A, uA_n, and finds that there are no outliers. The KBES then transfers the validated primary type A variables, unvalidated type B,

uB_n, and secondary variables, v, to the mathematical validation routine. This routine carries out a least squares reconciliation of master variables. The results are presented in a Table 1 (of the program output) which compares the values of the raw variables (AUDITOR) with the validated ones (INFO VALIDATOR). The validated primary variables are passed on to the SIMULATOR which validates the secondary variables. All the validated variables are presented in a table.

The results of the optimisation of the burner indicate that the optimum ammonia concentration is 11.39 % (V/V) compared to 10.96 % (V/V) at present correspnding to ammonia efficiencies of 93.34 and 93.27 % respectively. As the difference is ammonia efficiency is marginal, no change in operation of the burner is proposed.

The waste heat boiler optimisation suggests that the feed-water temperature to the economiser be brought down from 138 at present to 109 °C to increase the heat recovery in the WHB by 10.78 %.

6.3 Run Number 3

Run number 3 (Pg 118) is very similar to run 2 except that the operator feels that the ambient temperature of 13.8 °C is not correct. The operator refers to the Met Office database and inputs a value of 18 °C. Validation of the primary variables is then carried out.

6.4 Run Numbers 4 and 5

In Run number 4 (Pg 119) the operator needs to find the operating strategy for plant number 2. The KBES finds that the tailgas temperature is an outlier. The low-level fault diagnosis is used to find out the possibility of faults in the absorption system. When the operator finds that the acid circulation pumps have tripped he confirms that the pumps are not running normally. The KBES advises the operator to rectify this fault and then optimise the strategy of plant operation.

If on the other hand the operator confirms that there are no faults in the acid circulation system, as in Run number 5 (Pg 120-123), then the KBES proceeds to validate the rest of the variables on the conclusion that the the oxygen analyser is faulty. A default value of 0.7 % (V/V) is used for the oxygen content in the tail-gas. Simulation and optimisation of the operating strategy then follow.

The optimum ammonia concentration and efficiency are 11.43 % (V/V) and 93.2 %. As there is approximately 0.5% to be gained in terms of ammonia efficiency, it is proposed to increase the ammonia concentration to the optimum that is suggested by the OPTIMISER.

The optimum economiser water temperature is 107°C against the present temperature of 137.9°C. It is therefore proposed to bring down the temperature to the optimum suggested by the OPTIMISER thereby increasing the energy recovery by 11.32 %.

6.5 Run Number 6

Run number 6 (Pg 124-127) is the optimisation of operating stategy of plant number 3. The KBES first checks the master variables and finds that there

are no outliers. On checking the primary type A variables, uA_n, the KBES finds that there no outliers except for the oxygen in the tail-gas. The ratio of Oxygen to NO_x has been correlated for the nitric acid plants. Using an empirical correlation and the NO_x measurement the oxygen content is calculated. The empirical formula for the calculation has **not** be incorporated in the INFO VALIDATOR source code in APPENDIX 2. The validation is followed by simulation and the optimisation of operating strategy.

6.6 Run Numbers 7 and 8

Run number 7 (Pg 128) demonstrates the ability of KBES to recognise the state in plant operation when the operating rate is being changed. The datafile for this run was prepared at a time when the ammonia rate in plant number 3 was suddenly increased. The KBES calculates that the ammonia to acid ratio is 337 NM3/Te as against a normal range of 200 to 245. The KBES queries the operator whether there have been any upsets or rate changes. When the operator replies in the affirmative the validation is aborted.

Run number 8 (Pg 129) demonstrates the pitfalls of validating mass flowrates when there has been a sudden step change of operating rate. Despite the warning that the ammonia to acid ratio is high and the acid flowrate (master variable) is an outlier, the operator chooses to continue the validation procedure. The mathematical validation produces negative values for primary and secondary air rates and equally absurd values for the ammonia and acid rates !

6.7 Run Numbers 9 and 10

Run number 9 (Pg 130) shows the ability of the KBES to detect an outlying temperature master variable. The KBES finds that the mixed gas temperature is an outlier and advices the operator to abort the validation procedure.

Run number 10 (Pg 131) gives the validation results if contrary to the advice of the KBES, the operator chooses not to abort the validation procedure . As in run number 8, the mathematical validation produces absurd results. Hence if an outlying master variables is detected, it is safe to abort the validation procedure.

```
RUN
RUN NUMBER :1

**************************************************************************
                NITRIC ACID AUDITOR PRIMARY VALIDATOR
                  KNOWLEDGE BASED VALIDATION
                     VERSION 3, 15 AUG 1987
**************************************************************************

Which plant's measurements did you want validate (No.2 or 3)? 3

***************CHECK ON STARTUP OR SHUTTING DOWN CONDITIONS*******
Is the plant being started up or shutdown (Y/N) ?y

Software only handles steady state conditions


Validation aborted
Ok
```

```
RUN
RUN NUMBER :2

**************************************************************************
                NITRIC ACID AUDITOR PRIMARY VALIDATOR
                  KNOWLEDGE BASED VALIDATION
                     VERSION 3, 15 AUG 1987
**************************************************************************

Which plant's measurements did you want validate (No.2 or 3)? 3

***************CHECK ON STARTUP OR SHUTTING DOWN CONDITIONS*******
Is the plant being started up or shutdown (Y/N) ?n

****************CHECK ON STEADY STATE CONDITIONS****************
Has the plant been in steady state conditions for atleast 30 mins (Y/N)?y

***************CHECK ON MASTER MEASUREMENTS********************
Checked all the Master Variables    Outliers Detected= 0

************CHECK ON THE REST OF THE PRIMARY VARIABLES*******************
The ambient temperature is 13.8
Does the ambient temperature seem OK? (Y/N)? y
All primary variables, type A checked

**************************************************************************
                NITRIC ACID AUDITOR VALIDATOR
                  MATHEMATICAL VALIDATION
                     VERSION 3, 15 AUG 1987
**************************************************************************
Validated NH3 Flow NM3/H              = 9081
Validated Air Flow NM3/H              = 73727
Validated Acid Flow Te/H              = 38.89
Validated Sec Air Flow NM3/H          = 13795
Validated Process Water Flow M3/H     = 8.56

                TABLE 1. VALIDATION OF PRIMARY VARIABLES
                ****************************************
                                          AUDITOR        VALIDATOR
COMPRESSOR SUCTION PRESSURE PSIA           13.978          14.699
COMPRESSOR DISCHARGE PRESSURE PSIA         75.88           73.499
TAILGAS PRESSURE TO TURBINE PSIA           49.995          49.99
COMPRESSOR SUCTION TEMP DEG C              13.803          13.803
AMMONIA PRESSURE TO MIXER PSIG             64.21           61.218
PROCESS WATER M3/H                         8.01            8.56
PRIMARY AIR TEMP TO MIXER DEG C            155.11          155.19
TAILGAS TEMP EX ABS. TOWER DEG C           36.984          36.98
MIXED GAS TEMP DEG C                       138.06          139.36
AMMONIA TEMP EX S/HEATER DEG C             35.776          36.35
WATER TEMP TO ECON. DEG C                  133.21          133.21
NOX AT REACTOR INLET PPM                   4962.4          4962
O2 IN THE TAIL-GAS  %                      .7536           .7536
PRIMARY AIR  NM3/H                         72034           73727
AMMONIA FEED NM3/H                         8990            9081
SECONDARY AIR NM3/H                        11275           13795
HNO3 MASS FLOW TE/H                        39.486          38.89
HNO3 ACID STRENGTH % W/W                   58.6            58.6
00:00:59
Ok
```

RUN NUMBER : 2

```
**************************************************************************
                    NITRIC ACID PROCESS SIMULATOR
                        VERSION 3, 15 JAN 1987
**************************************************************************

          NITRIC ACID PLANT NUMBER 3

          COMPOSITION OF STREAM  1

     NITROGEN          KMOL/H= 2600.21
     OXYGEN            KMOL/H= 691.19
     AMMONIA           KMOL/H= 0
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     ------------------------------
     TOTAL FLOW        KMOL/H= 3291.4
     ------------------------------
     TEMPERATURE             DEG C= 13.64
     PRESSURE                  ATA= 1
     SPECIFIC ENTHALPY     KC/KMOL= 93.52
     ENTHALPY                  KC= 307826.18

          COMPOSITION OF STREAM  2

     NITROGEN          KMOL/H= 2600.21
     OXYGEN            KMOL/H= 691.19
     AMMONIA           KMOL/H= 0
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     ------------------------------
     TOTAL FLOW        KMOL/H= 3291.4
     ------------------------------
     TEMPERATURE             DEG C= 219.48
     PRESSURE                  ATA= 5
     SPECIFIC ENTHALPY     KC/KMOL= 1545.49
     ENTHALPY                  KC= 5086842.72

          COMPOSITION OF STREAM  3

     NITROGEN          KMOL/H= 2600.21
     OXYGEN            KMOL/H= 691.19
     AMMONIA           KMOL/H= 0
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     ------------------------------
     TOTAL FLOW        KMOL/H= 3291.4
     ------------------------------
     TEMPERATURE             DEG C= 155.19
     PRESSURE                  ATA= 5
     SPECIFIC ENTHALPY     KC/KMOL= 1086.3
     ENTHALPY                  KC= 3575469.46

          COMPOSITION OF STREAM  5

     NITROGEN          KMOL/H= 0
     OXYGEN            KMOL/H= 0
     AMMONIA           KMOL/H= 405.43
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     ------------------------------
     TOTAL FLOW        KMOL/H= 405.43
     ------------------------------
     TEMPERATURE             DEG C= 36.35
     PRESSURE                  ATA= 5.16
     SPECIFIC ENTHALPY     KC/KMOL= 248.98
     ENTHALPY                  KC= 100949.11

          COMPOSITION OF STREAM  6

     NITROGEN          KMOL/H= 2600.21
     OXYGEN            KMOL/H= 691.19
     AMMONIA           KMOL/H= 405.43
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     ------------------------------
     TOTAL FLOW        KMOL/H= 3696.84
     ------------------------------
     TEMPERATURE             DEG C= 138.67
     PRESSURE                  ATA= 5.09
     SPECIFIC ENTHALPY     KC/KMOL= 994.43
     ENTHALPY                  KC= 3676259.13

          COMPOSITION OF STREAM  7

     NITROGEN          KMOL/H= 1300.1
     OXYGEN            KMOL/H= 345.59
     AMMONIA           KMOL/H= 202.71
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     ------------------------------
     TOTAL FLOW        KMOL/H= 1848.42
     ------------------------------
```

TEMPERATURE	DEG C=	138.67
PRESSURE	ATA=	5.09
SPECIFIC ENTHALPY	KC/KMOL=	994.43
ENTHALPY	KC=	1838129.56

COMPOSITION OF STREAM 8

NITROGEN	KMOL/H=	1306.91
OXYGEN	KMOL/H=	99.01
AMMONIA	KMOL/H=	0
WATER VAPOR	KMOL/H=	304.07
NITRIC OXIDE	KMOL/H=	189.09
NITROGEN DIOXIDE	KMOL/H=	0
TOTAL FLOW	KMOL/H=	1899.1
TEMPERATURE	DEG C=	864.53
PRESSURE	ATA=	5.09
SPECIFIC ENTHALPY	KC/KMOL=	6357.27
ENTHALPY	KC=	12073120.95

COMPOSITION OF STREAM 9

NITROGEN	KMOL/H=	1306.91
OXYGEN	KMOL/H=	79.63
AMMONIA	KMOL/H=	0
WATER VAPOR	KMOL/H=	304.07
NITRIC OXIDE	KMOL/H=	150.34
NITROGEN DIOXIDE	KMOL/H=	38.74
TOTAL FLOW	KMOL/H=	1879.73
TEMPERATURE	DEG C=	200.91
PRESSURE	ATA=	4.94
SPECIFIC ENTHALPY	KC/KMOL=	1414.19
ENTHALPY	KC=	2658311.18

TABLE 2 : VALIDATION OF AUDITOR VARIABLES

VALIDATION OF PRIMARY VARIABLES

	AUDITOR	VALIDATOR
COMPRESSOR SUCTION PRESSURE PSIA	13.977	14.699
COMPRESSOR DISCHARGE PRESSURE PSIA	75.883	73.5
TAILGAS PRESSURE TO TURBINE PSIA	49.99	49.99
COMPRESSOR SUCTION TEMP DEG C	13.8	13.8
AMMONIA PRESSURE TO MIXER PSIG	64.21	61.21
PROCESS WATER M3/H	8.01	8.56
PRIMARY AIR TEMP TO MIXER DEG C	155.11	155.19
TAILGAS TEMP EX ABS. TOWER DEG C	36.98	36.98
MIXED GAS TEMP DEG C	138.05	139.36
AMMONIA TEMP EX S/HEATER DEG C	35.77	36.35
WATER TEMP TO ECON. DEG C	133.21	133.21
NOX AT REACTOR INLET PPM	4962	4962
PRIMARY AIR NM3/H	73263	73727
AMMONIA FEED NM3/H	9143	9081
SECONDARY AIR NM3/H	11275	13795
HNO3 MASS FLOW TE/H	39.48	38.89
HNO3 ACID STRENGTH % W/W	58.59	58.59

VALIDATION OF SECONDARY VARIABLES

	AUDITOR	VALIDATOR
BURNER OULET TEMPERATURE C	867.16	864.53
BOILER OUTLET TEMPERATURE C	208.05	200.91

PLANT OPTIMISER

BURNER OPTIMISER
Present Operating NH3 Ratio v/v % = 10.96
Present Operating efficiency % = 93.2796
Optimum Ammonia Ratio v/v % = 11.39
Optimum ammonia efficiency achievable % = 93.3408

WASTE HEAT BOILER ENERGY RECOVERY OPTIMISER
Calculated Dewpoint for present conditions C= 99.92
Dewpoint approach temperature C= 15
Minimum allowable tube metal temperature C= 114.92
Present feedwater temperature C= 138
Optimum feedwater temperature C= 109
Optimised heat recovery KC/h= 2840097
Present heat recovery KC/h= 2563603
Additional heat recovery KC/h= 276494

COMPOSITION OF STREAM 9

NITROGEN	KMOL/H=	1306.91
OXYGEN	KMOL/H=	78.69
AMMONIA	KMOL/H=	0
WATER VAPOR	KMOL/H=	304.07
NITRIC OXIDE	KMOL/H=	148.45
NITROGEN DIOXIDE	KMOL/H=	40.63
TOTAL FLOW	KMOL/H=	1878.78
TEMPERATURE	DEG C=	181.5
PRESSURE	ATA=	4.94
SPECIFIC ENTHALPY	KC/KMOL=	1273.63
ENTHALPY	KC=	2392878.6

```
RUN
RUN NUMBER :3

**************************************************************************
                NITRIC ACID AUDITOR PRIMARY VALIDATOR
                  KNOWLEDGE BASED VALIDATION
                     VERSION 3, 15 AUG 1987
**************************************************************************

Which plant's measurements did you want validate (No.2 or 3)? 3

***************CHECK ON STARTUP OR SHUTTING DOWN CONDITIONS*******
Is the plant being started up or shutdown (Y/N) ?n

***************CHECK ON STEADY STATE CONDITIONS****************
Has the plant been in steady state conditions for atleast 30 mins (Y/N)?y

***************CHECK ON MASTER MEASUREMENTS********************
Checked all the Master Variables    Outliers Detected= 0

************CHECK ON THE REST OF THE PRIMARY VARIABLES******************
The ambient temperature is 13.8
Does the ambient temperature seem OK? (Y/N)? n
Do you have access to the ambient temp. from any other plant (Y/N)? n
Refer to met office database and input a value? 18
All primary variables, type A checked

**************************************************************************
                NITRIC ACID AUDITOR VALIDATOR
                  MATHEMATICAL VALIDATION
                     VERSION 3, 15 AUG 1987
**************************************************************************
Validated NH3 Flow NM3/H              = 9152
Validated Air Flow NM3/H              = 73187
Validated Acid Flow Te/H              = 39.07
Validated Sec Air Flow NM3/H          = 13255
Validated Process Water Flow M3/H     = 8.39

                  TABLE 1. VALIDATION OF PRIMARY VARIABLES
                  ****************************************
                                          AUDITOR        VALIDATOR
COMPRESSOR SUCTION PRESSURE PSIA           13.978          14.699
COMPRESSOR DISCHARGE PRESSURE PSIA         75.88           73.499
TAILGAS PRESSURE TO TURBINE PSIA           49.995          49.99
COMPRESSOR SUCTION TEMP DEG C              13.803          18
AMMONIA PRESSURE TO MIXER PSIG             64.21           61.218
PROCESS WATER M3/H                         8.01            8.39
PRIMARY AIR TEMP TO MIXER DEG C            155.11          155.38
TAILGAS TEMP EX ABS. TOWER DEG C           36.984          36.98
MIXED GAS TEMP DEG C                       138.06          139.2
AMMONIA TEMP EX S/HEATER DEG C             35.776          37.52
WATER TEMP TO ECON. DEG C                  133.21          133.21
NOX AT REACTOR INLET PPM                   4962.4          4962
O2 IN THE TAIL-GAS  %                      .7536           .7536
PRIMARY AIR  NM3/H                         72034           73187
AMMONIA FEED NM3/H                         8990            9152
SECONDARY AIR NM3/H                        11275           13255
HNO3 MASS FLOW TE/H                        39.486          39.07
HNO3 ACID STRENGTH % W/W                   58.6            58.6
00:01:01
Ok
```

```
RUN
RUN NUMBER :4

**********************************************************************
                NITRIC ACID AUDITOR PRIMARY VALIDATOR
                  KNOWLEDGE BASED VALIDATION
                     VERSION 3, 15 AUG 1987
**********************************************************************

Which plant's measurements did you want validate (No.2 or 3)? 2

***************CHECK ON STARTUP OR SHUTTING DOWN CONDITIONS*******
Is the plant being started up or shutdown (Y/N) ?n

***************CHECK ON STEADY STATE CONDITIONS****************
Has the plant been in steady state conditions for atleast 30 mins (Y/N)?y

***************CHECK ON MASTER MEASUREMENTS********************
Checked all the Master Variables    Outliers Detected= 0

************CHECK ON THE REST OF THE PRIMARY VARIABLES*******************
The ambient temperature is 10.72
Does the ambient temperature seem OK? (Y/N)? y
DIAGNOSIS OF OUTLYING TAILGAS TEMPERATURE
Are all the acid circulation pumps running normally? (Y/N)n
Is the acid cooling system malfunctioning? (Y/N)n
The tailgas temperature is LOW as the acid circulation is abnormal
Rectify faults with absorption system prior to plant optimisation


Validation aborted
Ok
```

```
RUN
RUN NUMBER :5

*************************************************************************
                NITRIC ACID AUDITOR PRIMARY VALIDATOR
                  KNOWLEDGE BASED VALIDATION
                     VERSION 3, 15 AUG 1987
*************************************************************************

Which plant's measurements did you want validate (No.2 or 3)? 2

***************CHECK ON STARTUP OR SHUTTING DOWN CONDITIONS*******
Is the plant being started up or shutdown (Y/N) ?n

***************CHECK ON STEADY STATE CONDITIONS****************
Has the plant been in steady state conditions for atleast 30 mins (Y/N)?y

***************CHECK ON MASTER MEASUREMENTS********************
Checked all the Master Variables    Outliers Detected= 0

************CHECK ON THE REST OF THE PRIMARY VARIABLES*******************
The ambient temperature is 10.72
Does the ambient temperature seem OK? (Y/N)? y
DIAGNOSIS OF OUTLYING TAILGAS TEMPERATURE
Are all the acid circulation pumps running normally? (Y/N)y
Is the acid cooling system malfunctioning? (Y/N)n
The tailgas temperature  measurement faulty as the acid circulation is normal
Will use a default value of 36 C

All primary variables, type A checked

*************************************************************************
                NITRIC ACID AUDITOR VALIDATOR
                  MATHEMATICAL VALIDATION
                     VERSION 3, 15 AUG 1987
*************************************************************************
Validated NH3 Flow NM3/H              = 8532
Validated Air Flow NM3/H              = 75286
Validated Acid Flow Te/H              = 39.61
Validated Sec Air Flow NM3/H          = 11904
Validated Process Water Flow M3/H     = 7.53

                  TABLE 1. VALIDATION OF PRIMARY VARIABLES
                  ****************************************
                                          AUDITOR        VALIDATOR
COMPRESSOR SUCTION PRESSURE PSIA           14.358          14.358
COMPRESSOR DISCHARGE PRESSURE PSIA         76.98           71.79
TAILGAS PRESSURE TO TURBINE PSIA           56.461          46.79
COMPRESSOR SUCTION TEMP DEG C              10.722          10.722
AMMONIA PRESSURE TO MIXER PSIG             65.81           62.811
PROCESS WATER M3/H                         7.9             7.53
PRIMARY AIR TEMP TO MIXER DEG C            138.8           138.47
TAILGAS TEMP EX ABS. TOWER DEG C           27.772          36
MIXED GAS TEMP DEG C                       126.2           127.74
AMMONIA TEMP EX S/HEATER DEG C             50.42           48.11
WATER TEMP TO ECON. DEG C                  144.33          144.32
NOX AT REACTOR INLET PPM                   3512.5          3512
O2 IN THE TAIL-GAS  %                      .7642           .7642
PRIMARY AIR  NM3/H                         76416           75286
AMMONIA FEED NM3/H                         9316            8532
SECONDARY AIR NM3/H                        12144           11904
HNO3 MASS FLOW TE/H                        39.222          39.61
HNO3 ACID STRENGTH % W/W                   59              59
00:01:15
Ok
```

```
system
RUN NUMBER : 5

**************************************************************************
                    NITRIC ACID PROCESS SIMULATOR
                       VERSION 3, 15 JAN 1987
**************************************************************************

          NITRIC ACID PLANT NUMBER 2

          COMPOSITION OF STREAM  1

     NITROGEN          KMOL/H= 2655.2
     OXYGEN            KMOL/H= 705.81
     AMMONIA           KMOL/H= 0
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     -------------------------------
     TOTAL FLOW        KMOL/H= 3361.01
     -------------------------------
     TEMPERATURE                DEG C= 10.56
     PRESSURE                     ATA= .97
     SPECIFIC ENTHALPY        KC/KMOL= 72
     ENTHALPY                      KC= 242008.71

          COMPOSITION OF STREAM  2

     NITROGEN          KMOL/H= 2655.2
     OXYGEN            KMOL/H= 705.81
     AMMONIA           KMOL/H= 0
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     -------------------------------
     TOTAL FLOW        KMOL/H= 3361.01
     -------------------------------
     TEMPERATURE                DEG C= 214.18
     PRESSURE                     ATA= 4.88
     SPECIFIC ENTHALPY        KC/KMOL= 1507.55
     ENTHALPY                      KC= 5066906.35

          COMPOSITION OF STREAM  3

     NITROGEN          KMOL/H= 2655.2
     OXYGEN            KMOL/H= 705.81
     AMMONIA           KMOL/H= 0
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     -------------------------------
     TOTAL FLOW        KMOL/H= 3361.01
     -------------------------------
     TEMPERATURE                DEG C= 138.47
     PRESSURE                     ATA= 4.88
     SPECIFIC ENTHALPY        KC/KMOL= 967.64
     ENTHALPY                      KC= 3252276.19

          COMPOSITION OF STREAM  5

     NITROGEN          KMOL/H= 0
     OXYGEN            KMOL/H= 0
     AMMONIA           KMOL/H= 380.91
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     -------------------------------
     TOTAL FLOW        KMOL/H= 380.91
     -------------------------------
     TEMPERATURE                DEG C= 48.11
     PRESSURE                     ATA= 5.27
     SPECIFIC ENTHALPY        KC/KMOL= 352.9
     ENTHALPY                      KC= 134428.08

          COMPOSITION OF STREAM  6

     NITROGEN          KMOL/H= 2655.2
     OXYGEN            KMOL/H= 705.81
     AMMONIA           KMOL/H= 380.91
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     -------------------------------
     TOTAL FLOW        KMOL/H= 3741.93
     -------------------------------
     TEMPERATURE                DEG C= 126.73
     PRESSURE                     ATA= 5.2
     SPECIFIC ENTHALPY        KC/KMOL= 905.01
     ENTHALPY                      KC= 3386496.05

          COMPOSITION OF STREAM  7

     NITROGEN          KMOL/H= 1327.6
     OXYGEN            KMOL/H= 352.9
     AMMONIA           KMOL/H= 190.45
     WATER VAPOR       KMOL/H= 0
     NITRIC OXIDE      KMOL/H= 0
     NITROGEN DIOXIDE  KMOL/H= 0
     -------------------------------
     TOTAL FLOW        KMOL/H= 1870.96
```

TEMPERATURE	DEG C=	126.73
PRESSURE	ATA=	5.2
SPECIFIC ENTHALPY	KC/KMOL=	905.01
ENTHALPY	KC=	1693248.02

COMPOSITION OF STREAM 8

NITROGEN	KMOL/H=	1334.53
OXYGEN	KMOL/H=	121.76
AMMONIA	KMOL/H=	0
WATER VAPOR	KMOL/H=	285.68
NITRIC OXIDE	KMOL/H=	176.58
NITROGEN DIOXIDE	KMOL/H=	0
TOTAL FLOW	KMOL/H=	1918.58
TEMPERATURE	DEG C=	800.71
PRESSURE	ATA=	5.2
SPECIFIC ENTHALPY	KC/KMOL=	6347.45
ENTHALPY	KC=	12178104.4

COMPOSITION OF STREAM 9

NITROGEN	KMOL/H=	1334.53
OXYGEN	KMOL/H=	102.13
AMMONIA	KMOL/H=	0
WATER VAPOR	KMOL/H=	285.68
NITRIC OXIDE	KMOL/H=	137.31
NITROGEN DIOXIDE	KMOL/H=	39.26
TOTAL FLOW	KMOL/H=	1898.94
TEMPERATURE	DEG C=	201.91
PRESSURE	ATA=	4.94
SPECIFIC ENTHALPY	KC/KMOL=	1419.06
ENTHALPY	KC=	2694728.21

TABLE 2 : VALIDATION OF AUDITOR VARIABLES

VALIDATION OF PRIMARY VARIABLES

	AUDITOR	VALIDATOR
COMPRESSOR SUCTION PRESSURE PSIA	14.357	14.357
COMPRESSOR DISCHARGE PRESSURE PSIA	76.981	71.79
TAILGAS PRESSURE TO TURBINE PSIA	56.46	46.79
COMPRESSOR SUCTION TEMP DEG C	10.72	10.72
AMMONIA PRESSURE TO MIXER PSIG	65.81	62.81
PROCESS WATER M3/H	7.9	7.53
PRIMARY AIR TEMP TO MIXER DEG C	138.8	138.47
TAILGAS TEMP EX ABS. TOWER DEG C	27.77	36
MIXED GAS TEMP DEG C	126.19	127.74
AMMONIA TEMP EX S/HEATER DEG C	50.41	48.11
WATER TEMP TO ECON. DEG C	144.33	144.33
NOX AT REACTOR INLET PPM	3512	3512
PRIMARY AIR NM3/H	77720	75286
AMMONIA FEED NM3/H	9475	8532
SECONDARY AIR NM3/H	12144	11904
HNO3 MASS FLOW TE/H	39.22	39.61
HNO3 ACID STRENGTH % W/W	59	59

VALIDATION OF SECONDARY VARIABLES

	AUDITOR	VALIDATOR
BURNER OULET TEMPERATURE C	868.46	800.71
BOILER OUTLET TEMPERATURE C	272.82	201.91

RUN NUMBER : 5

PLANT OPTIMISER

BURNER OPTIMISER
Present Operating NH3 Ratio v/v % = 10.17
Present Operating efficiency % = 92.7177
Optimum Ammonia Ratio v/v % = 11.43
Optimum ammonia efficiency achievable % = 93.1929

WASTE HEAT BOILER ENERGY RECOVERY OPTIMISER
Calculated Dewpoint for present conditions C= 98.28
Dewpoint approach temperature C= 15
Minimum allowable tube metal temperature C= 113.28
Present feedwater temperature C= 137.9
Optimum feedwater temperature C= 107
Optimised heat recovery KC/h= 2901560
Present heat recovery KC/h= 2606412
Additional heat recovery KC/h= 295148

COMPOSITION OF STREAM 9

NITROGEN	KMOL/H=	1334.53
OXYGEN	KMOL/H=	101.13
AMMONIA	KMOL/H=	0
WATER VAPOR	KMOL/H=	285.68
NITRIC OXIDE	KMOL/H=	135.32
NITROGEN DIOXIDE	KMOL/H=	41.26
TOTAL FLOW	KMOL/H=	1897.94
TEMPERATURE	DEG C=	181.5
PRESSURE	ATA=	4.94
SPECIFIC ENTHALPY	KC/KMOL=	1271.5
ENTHALPY	KC=	2413255.23

```
RUN
RUN NUMBER :6

*************************************************************************
                NITRIC ACID AUDITOR PRIMARY VALIDATOR
                  KNOWLEDGE BASED VALIDATION
                     VERSION 3, 15 AUG 1987
*************************************************************************

Which plant's measurements did you want validate (No.2 or 3)? 3

***************CHECK ON STARTUP OR SHUTTING DOWN CONDITIONS*******
Is the plant being started up or shutdown (Y/N) ?n

****************CHECK ON STEADY STATE CONDITIONS****************
Has the plant been in steady state conditions for atleast 30 mins (Y/N)?y

***************CHECK ON MASTER MEASUREMENTS********************
Checked all the Master Variables    Outliers Detected= 0

************CHECK ON THE REST OF THE PRIMARY VARIABLES******************
The ambient temperature is 13.91
Does the ambient temperature seem OK? (Y/N)? y
Check Oxygen analyser

DIAGNOSIS OF OUTLYING O2 MEASUREMENT
As the NOx measurement is normal,the O2 measurement can be
inferred from the NOx measurement

All primary variables, type A checked

*************************************************************************
                NITRIC ACID AUDITOR VALIDATOR
                  MATHEMATICAL VALIDATION
                     VERSION 3, 15 AUG 1987
*************************************************************************
Validated NH3 Flow NM3/H              = 9017
Validated Air Flow NM3/H              = 73507
Validated Acid Flow Te/H              = 38.95
Validated Sec Air Flow NM3/H          = 13834
Validated Process Water Flow M3/H     = 8.51

                  TABLE 1. VALIDATION OF PRIMARY VARIABLES
                  ****************************************
                                        AUDITOR        VALIDATOR
COMPRESSOR SUCTION PRESSURE PSIA         14.358          14.358
COMPRESSOR DISCHARGE PRESSURE PSIA       74.67           71.79
TAILGAS PRESSURE TO TURBINE PSIA         51.821          46.79
COMPRESSOR SUCTION TEMP DEG C            13.912          13.912
AMMONIA PRESSURE TO MIXER PSIG           64.54           61.542
PROCESS WATER M3/H                       8               8.51
PRIMARY AIR TEMP TO MIXER DEG C          155.25          153.84
TAILGAS TEMP EX ABS. TOWER DEG C         36.453          36.45
MIXED GAS TEMP DEG C                     136.98          139.56
AMMONIA TEMP EX S/HEATER DEG C           36.087          26.91
WATER TEMP TO ECON. DEG C                135.43          135.43
NOX AT REACTOR INLET PPM                 4765.9          4765
O2 IN THE TAIL-GAS  %                    .8665           .6999
PRIMARY AIR  NM3/H                       71952           73507
AMMONIA FEED NM3/H                       8994            9017
SECONDARY AIR NM3/H                      11441           13834
HNO3 MASS FLOW TE/H                      39.499          38.95
HNO3 ACID STRENGTH % W/W                 58.6            58.6
00:00:45
Ok
```

```
system
RUN NUMBER : 6

*************************************************************************
                    NITRIC ACID PROCESS SIMULATOR
                        VERSION 3, 15 JAN 1987
*************************************************************************

     NITRIC ACID PLANT NUMBER 3

     COMPOSITION OF STREAM  1

NITROGEN          KMOL/H= 2592.43
OXYGEN            KMOL/H= 689.12
AMMONIA           KMOL/H= 0
WATER VAPOR       KMOL/H= 0
NITRIC OXIDE      KMOL/H= 0
NITROGEN DIOXIDE  KMOL/H= 0
--------------------------------
TOTAL FLOW        KMOL/H= 3281.56
--------------------------------
TEMPERATURE                DEG C= 13.75
PRESSURE                     ATA= .97
SPECIFIC ENTHALPY        KC/KMOL= 94.32
ENTHALPY                      KC= 309542.99

     COMPOSITION OF STREAM  2

NITROGEN          KMOL/H= 2592.43
OXYGEN            KMOL/H= 689.12
AMMONIA           KMOL/H= 0
WATER VAPOR       KMOL/H= 0
NITRIC OXIDE      KMOL/H= 0
NITROGEN DIOXIDE  KMOL/H= 0
--------------------------------
TOTAL FLOW        KMOL/H= 3281.56
--------------------------------
TEMPERATURE                DEG C= 219.66
PRESSURE                     ATA= 4.88
SPECIFIC ENTHALPY        KC/KMOL= 1546.88
ENTHALPY                      KC= 5076207.41

     COMPOSITION OF STREAM  3

NITROGEN          KMOL/H= 2592.43
OXYGEN            KMOL/H= 689.12
AMMONIA           KMOL/H= 0
WATER VAPOR       KMOL/H= 0
NITRIC OXIDE      KMOL/H= 0
NITROGEN DIOXIDE  KMOL/H= 0
--------------------------------
TOTAL FLOW        KMOL/H= 3281.56
--------------------------------
TEMPERATURE                DEG C= 153.84
PRESSURE                     ATA= 4.88
SPECIFIC ENTHALPY        KC/KMOL= 1076.75
ENTHALPY                      KC= 3533457.46

     COMPOSITION OF STREAM  5

NITROGEN          KMOL/H= 0
OXYGEN            KMOL/H= 0
AMMONIA           KMOL/H= 402.56
WATER VAPOR       KMOL/H= 0
NITRIC OXIDE      KMOL/H= 0
NITROGEN DIOXIDE  KMOL/H= 0
--------------------------------
TOTAL FLOW        KMOL/H= 402.56
--------------------------------
TEMPERATURE                DEG C= 26.91
PRESSURE                     ATA= 5.18
SPECIFIC ENTHALPY        KC/KMOL= 164.78
ENTHALPY                      KC= 66337.83

     COMPOSITION OF STREAM  6

NITROGEN          KMOL/H= 2592.43
OXYGEN            KMOL/H= 689.12
AMMONIA           KMOL/H= 402.56
WATER VAPOR       KMOL/H= 0
NITRIC OXIDE      KMOL/H= 0
NITROGEN DIOXIDE  KMOL/H= 0
--------------------------------
TOTAL FLOW        KMOL/H= 3684.12
--------------------------------
TEMPERATURE                DEG C= 136.32
PRESSURE                     ATA= 5.11
SPECIFIC ENTHALPY        KC/KMOL= 977.06
ENTHALPY                      KC= 3599627.75

     COMPOSITION OF STREAM  7

NITROGEN          KMOL/H= 1296.21
OXYGEN            KMOL/H= 344.56
AMMONIA           KMOL/H= 201.28
WATER VAPOR       KMOL/H= 0
NITRIC OXIDE      KMOL/H= 0
NITROGEN DIOXIDE  KMOL/H= 0
--------------------------------
TOTAL FLOW        KMOL/H= 1842.06
```

TEMPERATURE	DEG C=	136.32
PRESSURE	ATA=	5.11
SPECIFIC ENTHALPY	KC/KMOL=	977.06
ENTHALPY	KC=	1799813.87

COMPOSITION OF STREAM 8

NITROGEN	KMOL/H=	1303.02
OXYGEN	KMOL/H=	99.76
AMMONIA	KMOL/H=	0
WATER VAPOR	KMOL/H=	301.92
NITRIC OXIDE	KMOL/H=	187.67
NITROGEN DIOXIDE	KMOL/H=	0
TOTAL FLOW	KMOL/H=	1892.38
TEMPERATURE	DEG C=	859.57
PRESSURE	ATA=	5.11
SPECIFIC ENTHALPY	KC/KMOL=	6356.77
ENTHALPY	KC=	12029459.03

COMPOSITION OF STREAM 9

NITROGEN	KMOL/H=	1303.02
OXYGEN	KMOL/H=	80.4
AMMONIA	KMOL/H=	0
WATER VAPOR	KMOL/H=	301.92
NITRIC OXIDE	KMOL/H=	148.95
NITROGEN DIOXIDE	KMOL/H=	38.71
TOTAL FLOW	KMOL/H=	1873.02
TEMPERATURE	DEG C=	200.68
PRESSURE	ATA=	4.94
SPECIFIC ENTHALPY	KC/KMOL=	1412.4
ENTHALPY	KC=	2645462.01

TABLE 2 : VALIDATION OF AUDITOR VARIABLES

VALIDATION OF PRIMARY VARIABLES

	AUDITOR	VALIDATOR
COMPRESSOR SUCTION PRESSURE PSIA	14.357	14.357
COMPRESSOR DISCHARGE PRESSURE PSIA	74.672	71.79
TAILGAS PRESSURE TO TURBINE PSIA	51.82	46.79
COMPRESSOR SUCTION TEMP DEG C	13.91	13.91
AMMONIA PRESSURE TO MIXER PSIG	64.54	61.54
PROCESS WATER M3/H	8	8.51
PRIMARY AIR TEMP TO MIXER DEG C	155.25	153.84
TAILGAS TEMP EX ABS. TOWER DEG C	36.45	36.45
MIXED GAS TEMP DEG C	136.97	139.56
AMMONIA TEMP EX S/HEATER DEG C	36.08	26.91
WATER TEMP TO ECON. DEG C	135.42	135.42
NOX AT REACTOR INLET PPM	4765	4765
PRIMARY AIR NM3/H	73180	73507
AMMONIA FEED NM3/H	9147	9017
SECONDARY AIR NM3/H	11441	13834
HNO3 MASS FLOW TE/H	39.49	38.95
HNO3 ACID STRENGTH % W/W	58.59	58.59

VALIDATION OF SECONDARY VARIABLES

	AUDITOR	VALIDATOR
BURNER OULET TEMPERATURE C	866.94	859.57
BOILER OUTLET TEMPERATURE C	207.88	200.68

RUN NUMBER : 6

PLANT OPTIMISER

BURNER OPTIMISER
Present Operating NH3 Ratio v/v % = 10.92
Present Operating efficiency % = 93.2395
Optimum Ammonia Ratio v/v % = 11.38
Optimum ammonia efficiency achievable % = 93.3399

WASTE HEAT BOILER ENERGY RECOVERY OPTIMISER
Calculated Dewpoint for present conditions C= 99.85
Dewpoint approach temperature C= 15
Minimum allowable tube metal temperature C= 114.85
Present feedwater temperature C= 137.9
Optimum feedwater temperature C= 109
Optimised heat recovery KC/h= 2830327
Present heat recovery KC/h= 2553884
Additional heat recovery KC/h= 276442

COMPOSITION OF STREAM 9

NITROGEN	KMOL/H=	1303.02
OXYGEN	KMOL/H=	79.45
AMMONIA	KMOL/H=	0
WATER VAPOR	KMOL/H=	301.92
NITRIC OXIDE	KMOL/H=	147.05
NITROGEN DIOXIDE	KMOL/H=	40.61
TOTAL FLOW	KMOL/H=	1872.07
TEMPERATURE	DEG C=	181.21
PRESSURE	ATA=	4.94
SPECIFIC ENTHALPY	KC/KMOL=	1271.39
ENTHALPY	KC=	2380141.57

```
RUN
RUN NUMBER :7

*************************************************************************
                NITRIC ACID AUDITOR PRIMARY VALIDATOR
                  KNOWLEDGE BASED VALIDATION
                     VERSION 3, 15 AUG 1987
*************************************************************************

Which plant's measurements did you want validate (No.2 or 3)? 3

***************CHECK ON STARTUP OR SHUTTING DOWN CONDITIONS*******
Is the plant being started up or shutdown (Y/N) ?N

***************CHECK ON STEADY STATE CONDITIONS****************
Has the plant been in steady state conditions for atleast 30 mins (Y/N)?Y
Ammonia to Acid Ratio of 337 NM3/Te is high, the usual range is 200 to 245!
Reckon that there has a process upsets or rate change recently, confirm? (y/N)Y
Wait for 30 mins of normal steady state operation


Validation aborted
Ok
```

```
RUN
RUN NUMBER :8

**************************************************************************
                NITRIC ACID AUDITOR PRIMARY VALIDATOR
                  KNOWLEDGE BASED VALIDATION
                     VERSION 3, 15 AUG 1987
**************************************************************************

Which plant's measurements did you want validate (No.2 or 3)? 3

***************CHECK ON STARTUP OR SHUTTING DOWN CONDITIONS*******
Is the plant being started up or shutdown (Y/N) ?N

****************CHECK ON STEADY STATE CONDITIONS****************
Has the plant been in steady state conditions for atleast 30 mins (Y/N)?Y
Ammonia to Acid Ratio of 337 NM3/Te is high, the usual range is 200 to 245!
Reckon that there has a process upsets or rate change recently, confirm? (y/N)N

***************CHECK ON MASTER MEASUREMENTS********************
Acid flow is 28.06 Te/h, measurement is an outlier.
Checked all the Master Variables    Outliers Detected= 1

STRONGLY RECOMMEND ABORTING VALIDATION DUE TO OUTLYING MASTER MEASUREMENT
AGREE? (Y/N)N
*************CHECK ON THE REST OF THE PRIMARY VARIABLES*******************
The ambient temperature is 17.84
Does the ambient temperature seem OK? (Y/N)? Y
Check Oxygen analyser

DIAGNOSIS OF OUTLYING O2 MEASUREMENT
As the NOx measurement is normal,the O2 measurement can be
inferred from the NOx measurement

All primary variables, type A checked

**************************************************************************
                NITRIC ACID AUDITOR VALIDATOR
                  MATHEMATICAL VALIDATION
                     VERSION 3, 15 AUG 1987
**************************************************************************
MAX £ ITERATIONS REACHED WITHOUT CONVERGENCE.
Validated NH3 Flow NM3/H              = 80566
Validated Air Flow NM3/H              =-565864
Validated Acid Flow Te/H              = 255.95
Validated Sec Air Flow NM3/H          =-628749
Validated Process Water Flow M3/H     = 205.39

                  TABLE 1. VALIDATION OF PRIMARY VARIABLES
                  ****************************************
                                          AUDITOR        VALIDATOR
COMPRESSOR SUCTION PRESSURE PSIA           14.165          14.699
COMPRESSOR DISCHARGE PRESSURE PSIA         77.2            73.499
TAILGAS PRESSURE TO TURBINE PSIA           50.086          50.08
COMPRESSOR SUCTION TEMP DEG C              17.841          17.841
AMMONIA PRESSURE TO MIXER PSIG             66.06           63.064
PROCESS WATER M3/H                         7.86            205.39
PRIMARY AIR TEMP TO MIXER DEG C            150.32          5.19
TAILGAS TEMP EX ABS. TOWER DEG C           39.114          39.11
MIXED GAS TEMP DEG C                       136.93          320.11
AMMONIA TEMP EX S/HEATER DEG C             40.172          2741.36
WATER TEMP TO ECON. DEG C                  132.85          132.85
NOX AT REACTOR INLET PPM                   4521.4          4521
O2 IN THE TAIL-GAS  %                      .8873           .69999
PRIMARY AIR  NM3/H                         76333          -565864
AMMONIA FEED NM3/H                         9484            80566
SECONDARY AIR NM3/H                        12544          -628749
HNO3 MASS FLOW TE/H                        28.066          255.95
HNO3 ACID STRENGTH % W/W                   58.6            58.6
00:01:46
Ok
```

```
RUN
RUN NUMBER :9

*************************************************************************
                  NITRIC ACID AUDITOR PRIMARY VALIDATOR
                    KNOWLEDGE BASED VALIDATION
                       VERSION 3, 15 AUG 1987
*************************************************************************

Which plant's measurements did you want validate (No.2 or 3)? 2

****************CHECK ON STARTUP OR SHUTTING DOWN CONDITIONS*******
Is the plant being started up or shutdown (Y/N) ?n

****************CHECK ON STEADY STATE CONDITIONS****************
Has the plant been in steady state conditions for atleast 30 mins (Y/N)?y

***************CHECK ON MASTER MEASUREMENTS********************
Mixed gas temperature is 122.87 C, measurement is an outlier.
Checked all the Master Variables    Outliers Detected= 1

STRONGLY RECOMMEND ABORTING VALIDATION DUE TO OUTLYING MASTER MEASUREMENT
AGREE? (Y/N)y


Validation aborted
Ok
```

```
RUN
RUN NUMBER :10

*************************************************************************
                NITRIC ACID AUDITOR PRIMARY VALIDATOR
                  KNOWLEDGE BASED VALIDATION
                     VERSION 3, 15 AUG 1987
*************************************************************************

Which plant's measurements did you want validate (No.2 or 3)? 2

***************CHECK ON STARTUP OR SHUTTING DOWN CONDITIONS*******
Is the plant being started up or shutdown (Y/N) ?n

***************CHECK ON STEADY STATE CONDITIONS***************
Has the plant been in steady state conditions for atleast 30 mins (Y/N)?y

***************CHECK ON MASTER MEASUREMENTS*******************
Mixed gas temperature is 122.87 C, measurement is an outlier.
Checked all the Master Variables    Outliers Detected= 1

STRONGLY RECOMMEND ABORTING VALIDATION DUE TO OUTLYING MASTER MEASUREMENT
AGREE? (Y/N)n
************CHECK ON THE REST OF THE PRIMARY VARIABLES******************
The ambient temperature is 11.74
Does the ambient temperature seem OK? (Y/N)? y
Check Oxygen analyser

DIAGNOSIS OF OUTLYING O2 MEASUREMENT
As the NOx measurement is normal,the O2 measurement can be
inferred from the NOx measurement

All primary variables, type A checked

*************************************************************************
                NITRIC ACID AUDITOR VALIDATOR
                  MATHEMATICAL VALIDATION
                     VERSION 3, 15 AUG 1987
*************************************************************************
MAX £ ITERATIONS REACHED WITHOUT CONVERGENCE.
Validated NH3 Flow NM3/H              =-263
Validated Air Flow NM3/H              = 113440
Validated Acid Flow Te/H              = 13.53
Validated Sec Air Flow NM3/H          = 54708
Validated Process Water Flow M3/H     =-14.42

                TABLE 1. VALIDATION OF PRIMARY VARIABLES
                ****************************************
                                          AUDITOR        VALIDATOR
COMPRESSOR SUCTION PRESSURE PSIA           14.541          14.541
COMPRESSOR DISCHARGE PRESSURE PSIA         78.47           72.705
TAILGAS PRESSURE TO TURBINE PSIA           59.344          47.7
COMPRESSOR SUCTION TEMP DEG C              11.746          11.746
AMMONIA PRESSURE TO MIXER PSIG             66.18           63.186
PROCESS WATER M3/H                         7              -14.42
PRIMARY AIR TEMP TO MIXER DEG C            148.62          126.36
TAILGAS TEMP EX ABS. TOWER DEG C           36.519          36.51
MIXED GAS TEMP DEG C                       122.87          145.78
AMMONIA TEMP EX S/HEATER DEG C             52.527          8016.92
WATER TEMP TO ECON. DEG C                  144.32          144.32
NOX AT REACTOR INLET PPM                   3607.4          3607
O2 IN THE TAIL-GAS  %                      .8107           .69999
PRIMARY AIR  NM3/H                         70879           113440
AMMONIA FEED NM3/H                         8572           -263
SECONDARY AIR NM3/H                        11318           54708
HNO3 MASS FLOW TE/H                        37.822          13.53
HNO3 ACID STRENGTH % W/W                   59.95           59.95
00:01:31
Ok
```

7 Conclusions and Recommendations

A methodology using a process measurement database together with a process simulator for optimising the operating strategy of a chemical process has been successfully developed.

The method first checks the validity of various measurements of the process variables required for the running of the process simulator using human expertise and the laws of conservation of mass and energy. The results of the process simulator are used for validating the rest of the measured variables to show the true state of operation of the process. The validated measurements and other unmeasured parameters calculated by the simulator are used to establish the need for changing the operating parameters of the process to optimise the use of raw materials, utilities and energy. The process operators are advised if there is a need to change the strategy of operation to achieve the optimum results.

In its present form the methodology is for off-line optimisation and is used in conjunction with an regulatory control system. The set points of the regulatory control system are reset to meet the recommendations of the optimum operating strategy.

The software is easy to use and as its architecture is modular it is possible to adapt it to situations where there are changes in the optimisation goals to match changes in business objectives. That is, the objective function can be changed to meet the demands of a changing economic environment. The scope of the OPTIMISER at present covers the optimisation of the ammonia efficiency in the burner and the energy recovery in the waste heat boiler. If for financial

reasons it is necessary to optimise on the platinum losses in addition to the ammonia efficiency in the burner, the objective function for the burner optimisation could be suitably modified to simultaneously optimise platinum losses and ammonia efficiency. Hence the methodology is used to bridge the gap between business objectives and plant operation.

Though human operators are able to control processes and produce products of suitable quality the individual process operator is bound to have his own variation of control strategy which could actually be in subtle conflict with the operating company's business objective without either the company or the operator realising it. These variations could end up in situations where certain operators may produce a product better than the quality specifications but at the same time using more energy or fuel than is required for the product that meets the quality specifications exactly. However if the methodology developed in this research is implemented, it will promote the use of a uniform operating strategy that truly meets the operating company's business objectives.

The methodology also helps in monitoring the process instrumentation as well as carrying out the main goal of optimisation. By comparing the results of validation with the process measurements gross errors in instrument measurements are detected and action by instrument personnel is initiated.

Another feature of the methodology is that the SIMULATOR and OPTIMISER software, if required, can be used as stand alone programs. They can used for studying the benefits or pitfalls of changing the operating strategy, especially when raw material quality changes.

A potential benefit of the methodology is that the mass balance reconciliation method of the primary INFO VALIDATOR can also be used to prepare production reports or statements after mass reconciliation of the raw materials and the products. This will be of great benefit to production sites where there are integrated manufacturing facilities and captive production and consumption of materials and energy.

7.1 Recommendations for future research

The present methodology is suitable for off-line optimisation of the operating strategy but it can be extended to on-line use. Off-line optimisation has been criticised for the time lag between the diagnosis of sub-optimal conditions and the correction of the variables responsible for those sub-optimal conditions. In addition it is feared that sometimes the recommendations of the optimisation packages may not be seriously implemented by the process operators. Hence the possibility of extending this research to on-line optimisation may be worth considering.

As the practice of process optimisation in the present research is concerned with the operating strategy rather than regulatory (dynamic) control, one can continue to use the existing steady state SIMILATOR and OPTIMISER but the INFO VALIDATOR would require modification if on-line optimisation is desired. The present INFO VALIDATOR makes use of a knowledge-based validation system which requires a dialogue with the process operator, making it unsuitable for on-line optimisation. To eliminate the requirement of a dialogue

with operators the expert system will have to be programmed with "deeper" knowledge to cope with the absence of the process operator and to incorporate an integrated fault diagnosis system.

Deep knowledge is knowledge that encompasses and accounts for the physical structure and comprehensive behaviour of a system. When knowledge is called either "deep" or "shallow", some implicit model is always assumed, even if it is not explicitly mentioned (Guida, 1985). For example, knowledge regarding physical laws and design principles of a system is considered deep knowledge when contrasted with knowledge about the system's function, operation or use. The implication of not having the assistance of operators to observe plant faults will therefore force us to use more quantitative knowledge about a system. An example of the use of quantitative knowledge in knowledge based validation (Section 4.3.1, item (ix)) is the use of the correlated vapour pressure equation (physical laws) for validating the temperature of economiser feedwater using the deaerator pressure. Another example is the use of the compression ratio (design principle) of the compressor at normal operating capacities to validate the discharge pressure when the suction pressure is known.

To implement on-line optimisation of operating strategy the process control and the optimisation software have to be adequately interfaced with the hardware to facilitate the two-way flow of information. The hardware will have to be planned carefully when the plant is being designed. Retrofitting additional hardware to collect and feedback information for the above will certainly be an expensive proposition. However, the criticism of time lags and incomplete or

incorrect implementation can be answered if the off-line optimiser is enhanced with software and hardware which are connected to the regulatory control system. This will automatically and precisely execute the recommendations of optimisation carried out on an off-line basis. Before embarking on research for modifying the present methodology for on-line use it is advisable to carry out a cost-benefit analysis to compare the on-line option with the off-line option.

By further developing the "low-level" fault detection system into a comprehensive fault detection system the process measurement validation can be integrated with fault diagnosis. This will enhance the capability of the software as an process operating tool.

NOMENCLATURE.

a	Constant of the Redlich Kwong equation.
a	Initial NO partial pressure, bar.
A	Constant as defined by equation 3.7.
A	Area, m^2
A_g	Surface area of gauze per unit cross-section, m^2/m^2.
A1, A2.....A10	Constants in equation 5.1.
A_1 ,B_1, C_1, D_1	Constants of equations 3.10 and 3.12.
A_2 ,B_2, C_2	Constants of equation 3.14.
A_3, B_3, C_3, D_3	Constants of equations 3.24.
AIRFLO	Primary air volumetric flow, NM^3/h.
ACIDFLO	Acid mass flowrate, Te/h.
b	Constant of the Redlich Kwong equation.
b	Initial oxygen partial pressure, atm.
B	Constant as defined by equation 3.8.
C	Concentration, $kmol/m^3$.
C	Ammonia concentration in equation 5.1, % V/V.
C_p	Heat capacity at constant pressure or specific heat, kJ/kmol.
C_v	Heat capacity at constant volume kJ/kmol.
C_1,C_2	Constants in equation 3.61.
d	Platinum wire diameter, m.
d_i	Inside diameter of tube, m.
d_c	Diameter of coil, m.
d_o	Outside diameter of tube, m.
f_{gs}, f_{ts}	Fouling factors, m^2K/kW.

E1, E2,...E4	Constants in equations 5.5 and 5.6.
Ef	Ammonia efficiency %.
F	Liquid forced convection enhancement factor.
F	Ammonia flowrate in equation 5.1, kmol/h.
G	Mass flowrate, Kg/m²h.
G1, G2,...G6	Constants in equations 5.5 and 5.6.
h	Heat transfer coefficient, kW/m²K.
H	Enthalpy, kJ.
HR	Heat of reaction, kJ/kmol.
k	Thermal conductivity, kW/m K .
k	Ratio of specific heats, i.e. C_p / C_v.
k_g	Gas phase mass transfer coefficient, kmol/h.m².bar.
k_p	Reaction rate constant.
k_1, k_2	Forward and backward reaction rate constants of nitric oxide oxidation reaction.
K_E	Equilibrium constant.
K_n	Fraction of overall radiant heat received by a tube row.
K_4	Equilibrium constant in equation for NO_2 dimerisation.
m	Constant in equation 3.61.
M_f	Molecular weight of burner feed-gas.
$M_{s,n}$	Molar flowrate of component "n" in stream "s".
MT_s	Molar flowrate of stream "s".
MW_s, MW_n	Molecular weight of stream and component.
n	Polytropic exponent.

n_s	Number of platinum gauzes.
N_H	Tube row number in equation 3.65.
N_{Pr}	Prandtl number.
N_{Re}	Reynold's number.
N_{Sc}	Schmidt's number.
N_{St}	Stanton's number.
NH3FLO	Ammonia volumetric flow, Nm^3/h.
P	Pressure or partial pressure of gas, bar.
PROFLO	Process water flow, m^3/h.
PTG	Tail-gas Pressure, bar.
q, qp	Heat flux, kW/m^2.
Q	Rate of heat transfer, kW.
r_{NH3}	Mass transfer rate, kmol/h.
R	Gas Constant.
S	Sum of the square of the errors of measurement.
S_T	Transverse pitch in a tube bundle, m.
sp	Shaft Power of the compressor, kW.
y_{NH3}	Ammonia mole fraction in gas mixture.
T	Temperature, K.
T_{com}	Temperature of commencement of oxidation, K.
uA1, uA2,...	Primary variables, type A.
uB1, uB2,...	Primary variables, type B.
v1, v2,....	Secondary variables.
U	Overall heat transfer coefficient, kW/m^2 K.
v	Volume, specific volume of gas, m^3/ kmol.
V_{El}	Volume of element.
VP1, VP2	Vapour pressure of water vapour at compressor.

	suction and tailgas conditions, bar.
x	Fall in NO partial pressure, Bar.
X	Dryness Fraction.
$X_{s,n}$	Mole fraction of component "n" in stream "s".
W	Acid concentration % in equation 5.6.
z	Compressibility factor.
z	Length or depth, m.

Greek Symbols.

α	Absorptivity of surface or gas.
μ	Viscosity of fluid, CP.
ρ	Density of fluid, Kg/m^3.
σ	Surface tension, Dynes/cm.
σ	Stefan-Boltzman's constant.
θ	Residence Time in an element, h.
ϵ	Emissivity of radiating surface or gas.

Subscripts.

b	Nucleate boiling.
c	Convective.
c	Refers to the critical property.
cm	Refers to the critical property of a mixture.
d	Refers to developed area of tube.
g	Gas.
gs	Gauze support.
i	Inside, when referring to a tube.
ic	Inside, when referring to a helical coil.

l	Liquid.
o	Outside when referring to a tube.
OPT	Optimum.
n	Non-luminous, when used for heat transfer coefficient.
n	Component number.
N	Element number.
r	Refers to the reduced state.
r	Radiant, when used for heat transfer coefficient.
re	Radiant evaporator.
rm	Refers to the reduced state of a gas mixture..
s	Stream number.
s	Steam or water.
sat	Saturation.
tp	Two phase.
w	Wall.
wa	Economiser water.

Superscripts

E	Equilibrium.
0	Refers to the "ideal" state of a gas.

REFERENCES

Almasy, G.A., Sztano, T., Csillag G., Veress, G. ang Holderith, J., (1969). 3rd CHISA Congress, Paper D3.10, Marianske Lazne, Czechoslovakia.

Alty, J.M. and Coombs, M.J. (1984).Expert Systems-Concepts and Examples. pp.161-176. Manchester : NCC Publications.

Alyott, M.R., Ponton, J.W. and Lott,D.H., (1985). Process Systems Engineering. PSE '85: The Use of Computers in Chemical Engineering. IChemE Symposium Series No 92. pp 55-66. Cambridge.

Andow, P.K. and Lees, F.P., (1975). Trans. I. Ch. E., 53, 195.

Andow, P.K., (1985). Process Systems Engineering. PSE '85: The Use of Computers in Chemical Engineering. IChemE Symposium Series No 92. pp 145-156. Cambridge.

Andrew. S.P.S., Hanson D.,(1961). Chem. Eng. Sci. 14, 105.

Andrussow, Z., (1926). Angew Chem 39, 321.

Andrussow, Z., (1924). Angew Chem 10, 166.

Banares-Alcantara, R., (1985). DECADE : Design Expert for CAtalyst DEvelopment, Ph.d Thesis, Carnegie Mellon Univ.

Banares-Alcantara, R., et al. (1985). development of an Expert System for Physical Property Estimation. Comp.and Chem. Eng. 9(2) p.127.

Barner, H.E., and Adler, S.B., (1970). Ind. Eng. Chem. Fundam., 9, 521.

Barney, J.R., Ahluwalia R.S. and Johnson A.I., (1975). DYNSYS 2.0 Users Manual. The University of Western Ontario. London, Canada.

Barsamian, J.R., (1986). Chem. Eng. May 12, pp. 105-108.

Bashan, Y. and Handelsman, M., (1987). Chem. Eng. Jan 19, pp. 123-125.

Bellman, R.E., (1957). Dynamic programming, Princeton University Press, Princeton.

Bennett, S. and Linkens, D.A., (1982). Computer Control of Industrial Processes. IEE COntrol Engineering Series 21. Stevenage, UK: Peter Peregrinus Ltd.

Berenblut,, B. J., and Whitehouse, H.B., (1977). Chem. Engr., March, 175.

Berger and Perris. FLOWPACK II- A new Generation of System for the Steady State Process Flowsheeting. EFCE Conference "CACE 1979", April 1979, Montreux, Switzerland.

Beveridge, G.S.G. and Schechter, R.S., (1970). Optimisation: Theory and Practice. New York: McGraw-Hill.

Bodenstein, (1937). Trans. Electrochem. Soc.. 71, 353.

Box, G.E.P. and Wilson, K.B., J, Royal Stat. Soc., B13, 1 (1951).

Bradley, J.K., Drake, M.A., (1981) . Nitric Acid Technology. London: The Fertiliser Society.

Brotz, W., Schnur, F., Proc.of 1st European Symposiun on Chemical Engineering, Chemical Reaction Engineering, Amsterdam, May 1957.

Bullock, R.H., (1987). Chem. Eng., June 22, pp.143-146.

Busby J.A., Knapton A.G. and Budd A.E.R. (1978). Catalytic Processes in Nitric Acid Manufacture. London: The Fertiliser Society.

Butterworth, D. and Shock, R.A.W., 1982, Heat Transfer 1982, Proceedings of the Seventh International Heat Transfer Conference, MÜnchen, Fed. Rep. of Germany, 11-30.

Canfield, F.B., 1985, Chem. Eng. Prog., 81, 9, 31.

Chen, J.C., 1966, Ind. Eng. Chem. Proc. Des. Dev., **5**, 322-329.

Chester, D. et al. (1984). Computers in Engineering Advanced Automation: 1984 and beyond. In Gruver, W.A. ed. ASME p.45.

Chilton, T.H., (1960) Chem. Eng Prog. Monograph Series No.3.

Chueh, P.L., and Prausnitz, J.P., (1967). AIChE J., 13, 896

Connor, H., (1967). Plat. Metals Rev. 11(1), 2.

Dantzig, G., (1951). Activity Analysis of Production and Allocation, Koopman, T.C., ED., Wiley, New York.

Cleary, A.T., (1983). Mech. Eng. July, pp. 43-47.

Dean, D.E. and Stiel, L.I.,(1965). AIChE J., 11, p.526.

Dekker, H.,Snoeck, E. and Kramers, H., (1959). Chem. Eng. Sci., 11, 61.

Dekker, H., Blind, M.P.P. and Snoeck, E., (1961). Chem. Eng. Sci., 14, 115.

Demeersman, R. (1979). J. Comput. Appl. Math. 5, 277.

deSantis,R., Breedveld, G.J.F. and Prausnitz, J.M., (1974). Ind. Eng. Chem. Des. Dev., 13, 374.

Duda, R.O., et al., (1978). Development of the PROSPECTOR Consultation System for mineral Exploration, Final Report, SRI Projects 5821 and 6451. Menlo Park, CA : SRI International Inc.

Edminster and Lee, (1984). Applied Hydrocarbon Thermodynamics, Vol. 1, Houston, Tx: Gulf Publishing Co.

Efsthathiou, H.J., (1985). Expert Systems For Maintenance Tasks. Computing and Control Div. Colloquium on "Real Time Expert Systems in Process Control", 29 Nov 1985.

Emig, G., Wolhfarht, K., Hoffman, U., 1979, Computers and Chemical Engineering, 3, 143-150.

Ermenc, E.D., (1956). Chem. Eng. Prog., 52, 4, 149.

Evans, L.B., and co-workers. ASPEN, An Advanced System for Process Engineering, CACE 1979, Montreux, Switzerland.

Fair, J.R., (1980). Advanced Process Engineering, AIChE Monograph Ser., 76, (13),

Finley, H.F., (1987). Hyd. Proc. 66 (1), pp. 64-66.

Ford, J.R., (1981). Chem. Eng. Prog. 77 (9), 74.

Forgy, C.L., (1981). OPS5 Manual, Technical Report CMU-CS-81-135, Carnegie Mellon University.

Forster, H.K., Zuber, N., AIChE J., **1** , 531-535

Fourre, J.P., (1968). Critical Path Scheduling: A practical Appraisal of PERT. American Management Association.

Fowler, J.R., (1981). Chem. Eng. Prog. 77 (9), 74.

Freidman M. and Savage L.S., (1947). Selected Techniques of Statistical Analysis, New York: McGraw-Hill.

Ganapathy, V., 1982, Applied Heat Transfer, PenWell Books, Tulsa.

Govind, R., Powers G.J., (1981). AIChe Journal, 27(3), p.429.

Grimes, L., et al. (1982). Chem. Eng. Commun., 14, p.339.

Guerreri, G. and Prausnitz, J.P., (1973). Process Tech. Int. 18(4), 209.

Guida, G., (1985). Computing and Control Div. Colloquium on "Real Time Expert Systems in Process Control" , 29 Nov 1985.

Hancock, H., (1960). Theory of Maxima and Minima, New York: Dover Publications.

Harrow, P., (1983). Computer-Aided Engineering Journal. Nov 1983. pp. 16-24.

Harvin, R.L., Leray, D.G., Roudier, L.R., (1978). Single or Dual pressure Nitric Acid Process: An Objective Comparison. 71st Annual Meeting of the American Institute of Chemical Engineers, Maimi, Florida.

Haspel, D. and Taunton, C., (1986). Expert Systems and Optimisation in Process Control. Mamdani, A., and Efstathiou, J., eds., p. 53. London: Technical Press.

Heck, R.M., Bonacci J.C., Hatfield, W.R. and Hsuing, T.H. (1982). Ind. eng. Chem. Des. Dev., 21, pp 73-79.

Hesky, H., (1961) Chem-Ing-Tech, 33, 27.

Himmelblau D.M., (1985). Process Systems Engineering. PSE '85: The Use of Computers in Chemical Engineering. IChemE Symposium Series No 92. Cambridge.

Hines, J.G., (1978). Online surveilliance Techniques, Past, Present and Future. Proceedings of the Symposium: Online Surveillance and Monitoring of Process Plant. 26-28 Sept. The City University of London, London.

Hoffman, Muller, R., Messen, R., and Stevern. (1966) Regeln, 9, 233.

Holland, F.A., et al., (1970). Heat Transfer. pp.336-339. London: Hieneman Educational Books.

Holzmann, H., (1967). Chemie-Ing-Tech 39 (2) 89.

Hopfer, K. and Dayasagar, I., (1980). Recent Adv. Inorg. Acid Proc. Lect. Ser., Indian Chem. Manuf. Assoc., PP 45-63, Bombay.

Hottel, H.C., and Mangelsdorf, H.G., (1935) Trans. Am. Inst. Chem. Engrs., £1, 517-549.

Hunt, L. B.,(1958). Platinum Metals Rev. 2 (4) 129.

Iri, M., Aoki, K., O'Shima, E., and Matsuyuma, H., (1980). J. Operations

Research Soc. (Japan), 23, 295.

Iri, M., Aoki, K., O'Shima, E., and Matsuyuma, H., (1981). Comp. Chem. Eng., 3, 489.

Janna, W.S., (1986). Engineering Heat Transfer, PWS Publishers, Boston, Ma.

Jelen, F.C., (1970). Cost and Optimisation Engineering. New York: McGraw-Hill.

Joglekar, G.S. and Reklaitis, G.V., (1984). Comp. Chem. Eng. 8, pp 315-327

Johnson, A.I., Peters. (1979). The modular approach to systems analysis and design (GEMCS Manual). Montreal, Canada: McMaster University.

Joris, P., and Kalitventzeff, B., (1987). Proc. XVIII congress: The use of Computers in Chemical Engineering, Sicily. p 41.

Kane, L. (ed.) (1980). Process Control and Optimisation Handbook for the Hydrocarbon Processing Industries, p. 14. Houston, USA: Gulf Publishing Company.

Kane, L. (ed.) (1987). 1987 Advanced Process Control Handbook II, Hydrocarbon Processing, 66 (3), pp 57-109.

Keleti ed. (1985a). Fertilizer Science and Technology Series. Volume 4. Nitric Acid and Fertilizer Nitrates, p.3, New York: Marcel Dekker.

Keleti, ed. (1985b). Fertiliser Science and Technology Series. Vol. 4. Nitric Acid and Fertilizer Nitrates, pp.61-98. New York : Marcel Dekker.

Kesler, M.G. and Kessler, M.M., (1958). World Petroleum, 29, 8, pp 60-63.

Kerridge, A.E., (1987). Hydrocarbon Processing. 66 (9), pp. 97-105.

Kirk-Othmer, (1981a). Encyclopedia of Chemical Technology. 3rd Edition, Vol. 15, p 853.

Kirk-Othmer, (1981b). Encyclopedia of Chemical Technology, 3rd ed. Vol. 21, p.33.

Koukolik, M., Marek, J., Chem. Reaction Eng. Proc. 4th European Symp., (1968). Brussels, p 1.

Koukoulis, C., (1985). A Frame-based Method for Fault Diagnosis. Computing and Control Div. Colloquium on "Real Time Expert Systems in Process Control" , 29 Nov 1985.

Kulikowski, C.A., Weiss, S.M. (1982). Representation of Expert Knowledge for Consultation : the CASNET and EXPERT projects. In Szolovitz, P. ed. Artifical Intelligence in Medicine. Boulder : Westview Press.

Lackmeyer R.J., Kempfer, D.G., Proceedings of the 1977 Joint Automatic Control Conference, San Francisco, Ca., pp. 345-356.

Lebhaber, M., et al., (1974). Ind. Eng. Chem. Process Des. Develop. 13(1), 39.

Leesley, M.E., (1982a). Computer-aided Process Plant Design. Houston: Gulf publishing Co.

Leesley, M.E., (1982b). Computer-aided Process Plant Design. pp 1123-1182, Houston: Gulf publishing Co.

Leesley, M.E., (1982c). Computer-aided Process Plant Design. pp 536-545, Houston: Gulf publishing Co.

Leesley, M.E., (1982d). Computer-aided Process Plant Design. pp 696-706. Houston : Gulf Publishing Co.

Lindsay, R., et al. (1980). Applications of Artificial Intelligence for Chemical Interface : The DENDRAL project. New York : McGraw Hill.

Lutcha, J., Klemsa, J., and Holcak, B., (1985). Process Systems Engineering. PSE '85: The Use of computers in chemical engineering. IChemE Symposium Series No 92. pp 111-120. Cambridge.

Kirk-Othmer, (1981b). Encyclopedia of Chemical Technology, 3rd ed. Vol. 21, p.33.

Koukolik, M., Marek, J., Chem. Reaction Eng. Proc. 4th European Symp., (1968). Brussels, p 1.

Koukoulis, C., (1985). A Frame-based Method for Fault Diagnosis. Computing and Control Div. Colloquium on "Real Time Expert Systems in Process Control" , 29 Nov 1985.

Kulikowski, C.A., Weiss, S.M. (1982). Representation of Expert Knowledge for Consultation : the CASNET and EXPERT projects. In Szolovitz, P. ed. Artifical Intelligence in Medicine. Boulder : Westview Press.

Lackmeyer R.J., Kempfer, D.G., Proceedings of the 1977 Joint Automatic Control Conference, San Francisco, Ca., pp. 345-356.

Lebhaber, M., et al., (1974). Ind. Eng. Chem. Process Des. Develop. 13(1), 39.

Leesley, M.E., (1982a). Computer-aided Process Plant Design. Houston: Gulf publishing Co.

Leesley, M.E., (1982b). Computer-aided Process Plant Design. pp 1123-1182, Houston: Gulf publishing Co.

Leesley, M.E., (1982c). Computer-aided Process Plant Design. pp 536-545, Houston: Gulf publishing Co.

Leesley, M.E., (1982d). Computer-aided Process Plant Design. pp 696-706. Houston : Gulf Publishing Co.

Lindsay, R., et al. (1980). Applications of Artificial Intelligence for Chemical Interface : The DENDRAL project. New York : McGraw Hill.

Lutcha, J., Klemsa, J., and Holcak, B., (1985). Process Systems Engineering. PSE '85: The Use of computers in chemical engineering. IChemE Symposium Series No 92. pp 111-120. Cambridge.

Mah R.S., Stanley, G.M. and Downing, D.M. (1976). Ind. Eng. Chem. 15 (1) pp 175-183.

Martin, G. and Barbour, W. (1915). Industrial Nitrogen Coumpounds and Explosives, London: Crosby Lockwood.

McAdams, W. H., (1954a). Heat Transmission, 3rd ed., p. 228, McGraw-Hill, New York.

McAdams, W. H., (1954b). Heat Transmission, 3rd ed., pp. 82-85, McGraw-Hill, New York.

McGreavy C., (1985). Expert Systems in Process Plant Start-up. Computing and Control Div. Colloquium on "Real Time Expert Systems in Process Control" , 29 Nov 1985.

McKetta, J.J., ed. (1979).Encyclopedia of Chemical Processing and Design. Vol.10 p.171. New York and Basel : Marcel Dekker.

Michie, D. ed. (1983), Introductory Readings in Expert Systems. p. 3 . New York: Gordan and Breach.

Miller,A.M., et al. (1982). INTERNIST-I, an experimental computer-based Diagnostic Consultant for general Internal Medicine. New England Journal of Medicine, 307, pp.468-476.

Moore, R.l., et al. (1984). Expert Systems Applications in Industry. ISA '84 Internatinal Conference and Exhibit. Houston, Tx.

Motard, R.L., Lee, H.M., (1971). CHESS, Chemical Engineering User's Guide. 3rd. ed. Houston: University of Houston.

Motard, R.L., (1983). Computer Technology in Process Engineering Systems. Comp. Chem. Eng. 7 (4), pp 483-491.

Nakamura, R., Breedveld, G.J.F. and Prausnitz, J.M., (1976). Ind. Eng. Chem. Des. Dev., 15, 557.

Norman, P., Voon, Y.W., (1985). Proceedings of the 4th International Conf. Eng. Software, p.4-73.

Overturf, B.W., et al., (1978). Ind. Eng.Chem. Process Des. Develop. 17, 161.

Palowitch, B.L., Kramer, M.A., (1985). American Control Conference, pp. 646-651.

Patterson, G.K.,Rossa, R.B., (1980). Comput. Chem. Eng. 4, 1.

Pignet, T. and Schmidt, L.D., (1975). Journal of Catalysis, 40, 212-225.

Pratt, C. J., Noyes, R. (1965). Nitrogen Fertilizer Chemical Processes, New York: Noyes Development Corp.

Rase, H.F., (1977). Chemical Reactor Design for Process Plants. Vol. 2: Case Studies and Design Data. pp 115-122, New York: John Wiley.

Redlich, O., Kwong, J.N.S., (1949).Chem. Rev., 44: 233.

Reid, R.C., Prausnitz, J.M., Sherwood, T.K., (1977a). The Properties of Gases and Liquids. 3rd edition. New York : McGraw Hill.

Rosen, E.M., Pauls, A.C., (1979). Computers Aided Chemical Process Design: The FLOWTRAN System, Computers and Chemical Engg., 1,(1), p 11.

Rudd D.F. and Watson C.C., (1968). Strategy of Process Engineering. New York: John Wiley .

Sargent R.W.H., (1983). Process Systems Engineering: Challenges and Constraints in Computer Science. Proceedings of the Second International Conference on the Foundations of Computer-aided Design, Westerberg, A.W., and Chien, H.H., Eds., pp 23-46.

Satterfield C.N., and Cortez D.H., (1970). Ind. Eng. Chem. Fund., 9, 613.

Shammas, N.C., (1983). Chem. Eng. (N.Y.), July 25, pp 81-84.

Shannon, A.E., (1975). AIIE Trans. 7(3), 289

Sherwood, T.K., Pigford, R.L., (1952). Absorption and Extraction, pp 368-375, New York: McGraw-Hill.

Shinskey, F.G. ed. (1977). Distillation Control for Productivity and Energy Conservation. New York: McGraw-Hill.

Shortliffe, E.H., (1976). Computer-based Medical Consultations.: MYCIN. New York : American Elsevier.

Soave, G.,(1972) Chem. Eng. Sci., 27, 1197.

Solomon, C.H. and Hodges, A.W., (1963). Brit. Chem. Eng., 8, 8, pp.551-555.

Springell J., (1985). Chem. Eng. Prog. 81 (9), 53.

Westerberg, A.W., Hutchinson, H.P., Motard, R.L. and Winter, P., (1979). Process Flowsheeting. p 24, Cambridge University Press: Cambridge.

Sriram, D. et al., (1985). Knowledge-based Expert Systems in Structural Design. Computers and Structures. Jan 1985.

Stiel, L.I., Thodos, G.,(1964). AIChE J., 10, p.26.

Stewart, W.E. ed. (1980). Dynamics and Modelling of Reactive Systems. Vol 44, Mathematical Research Series, New York: Academic Press.

Swenkar, A.G., (1964). Proc. 3rd Int. Measurements Conf. , Budapest. 1, 29.

Tarakad, R.R., Spencer, C.F. and Adler, S.B., (1979). Ind. and Eng. Chem. Des. Dev., 18, 4, 727.

Umeda, T., (1983). Computer Aided Process Synthesis. Comp. Chem. Eng. 7 (4), pp 279-309.

Vaclavek, V., (1969). Chem. Eng. Sci., 24, 947.

West, M.R., (1985). Process Systems Engineering, PSE 85, The Inst. Chem. Engr. Symp. Ser. No 92. p.263.

Williams,, T.J., (1983). Developments in Hierarchical Computer Control Systems as affecting manufacturing Systems of the Future. Proceedings of the 1st International Conference on Computer Applications in Production and Engineering. Amsterdam: North Holland Publishing.

Welbourne, D., (1968). Proc. IEE, 115, 1726,

Winter, P., (1981). Process Engineering, 62(6), 33

Wise, H. and French, M.F., (1954). J. Chem. Phys. 22, 1463.

Zawadski, J., (1950). Disc. Faraday Soc. 8 140.